

ANALYSIS OF LEATHER

AND

MATERIALS USED IN MAKING IT

BY

JOHN ARTHUR WILSON, Sc. D.
*President, John Arthur Wilson, Inc., Consulting Tanners
and Chemists, Milwaukee, Wis.*

AND

HENRY BALDWIN MERRILL, Ph. D.
*Chief Chemist, A. F. Gallun & Sons Corp.,
Milwaukee, Wis.*

FIRST EDITION

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK AND LONDON
1931

COPYRIGHT, 1931, BY THE
MCGRAW-HILL BOOK COMPANY, INC.

PRINTED IN THE UNITED STATES OF AMERICA

*All rights reserved. This book, or
parts thereof, may not be reproduced
in any form without permission of
the publishers.*

THE MAPLE PRESS COMPANY, YORK, PA.

PREFACE

The object of this book is to give, in convenient form, working directions for the analysis and testing of leather and all the more important materials used in making leather, brief discussions of the principles upon which the methods of analysis are based, shortcomings of the methods, common sources of error, and interpretations of the results obtained. Average or typical analyses, most of which were made in the authors' laboratories, are given, wherever possible, as illustrations.

The only other book in the English language having the same scope as this one is Procter's "Leather Industries Laboratory Book," published in 1908. The need for a book of this character has been increasingly felt since that time, especially since many important methods have been developed during the past twenty-three years. Because of the great variety of substances that a leather chemist is called upon to examine, in the absence of a book of this kind, he is forced to consult a large number of books for his methods of analysis. The leather chemist must, of course, possess a knowledge of the principles of analytic procedure far greater than it would be possible to present in a volume of this size. It has been found possible, however, to collect in this book sufficient information to permit him to analyze most of the materials that he is likely to encounter and to understand what he is doing and why.

This book had its inception in the laboratories of A. F. Gallun & Sons Corporation, where methods of analysis have been developed and collected for more than thirty years. To these methods the authors have added the methods of the American Leather Chemists Association and pertinent methods sponsored by recognized societies as well as methods taken from standard texts and the current literature or provided by other laboratories. In order to make the book as complete and generally useful as possible, the authors have included some methods with which

they have had little personal experience and trust that any unwitting display of ignorance on their part in such cases will be pardoned.

A work of this kind is so obviously a compilation that it seems unnecessary for the authors to disclaim credit for originating more than a fraction of the methods presented. The term "Authors' method" prefixed to a procedure merely indicates a method used and endorsed by the authors and not necessarily one which they have originated or developed. They have not felt obliged to credit every method to its ultimate source, excepting in those cases where a method is designated by the name of its author or where a new method has not yet found its way into textbooks.

The forms for calculating results, given with almost every determination, have been simplified, possibly at the expense of clarity in some cases, by combining some constant numerical factors. Many of these forms are valid only when the procedure is followed literally with respect to size of sample and aliquots, a point to be remembered. The 1929 atomic weights were used.

The Bibliography contains nearly 600 citations, but might have contained many thousands, if it were the authors' ambition to make it a complete bibliography of analytic chemistry. They have limited themselves to comparatively recent publications dealing primarily with the analysis of leather and materials encountered by the tannery chemist. The Bibliography was compiled prior to September, 1929, at which time the text was substantially complete. Only in a few cases has work published since that date been added.

Grateful acknowledgment is made of the courtesy of the American Leather Chemists Association, the American Public Health Association, the American Society for Testing Materials, and the Association of Official Agricultural Chemists for permission to reprint extracts from their official or tentative methods, and of Dr. W. M. Clark and The Williams & Wilkins Co. for permission to reproduce some of the tables from Clark's "The Determination of Hydrogen Ions." For the loan of illustrations or other assistance, the authors are also indebted to Bausch & Lomb Optical Co., Leeds & Northrup Co., La Motte Chemical Products Co., Henry L. Scott Co., Frank E. Randall, A. Wyzenbeek & Staff,

Hercules Powder Co., Arthur H. Thomas & Co., and Dr. Thomas Blackadder. The authors also wish to thank their coworkers for invaluable assistance, particularly Dr. R. G. Henrich, chemist in charge of the analytic laboratory of A. F. Gallun & Sons Corporation, and Miss Marie Kelnhofer, who typed the manuscript.

The value of chemical analysis in the control of tannery operations is now almost universally recognized. It is hoped that this book may be of assistance to those whose task it is to design and operate such control systems. May it also serve those who supply tanneries with their products and those who use the products of the tannery.

J. A. W.
H. B. M.

MILWAUKEE, WIS.,
August, 1931.

CONTENTS

	PAGE
PREFACE	v
CHAPTER I	
INTRODUCTION	1
CHAPTER II	
CHEMICAL ANALYSIS OF SKIN AND LEATHER	7
Sampling—Preparation of Sample for Analysis—Specific Gravity— Determination of Water—Determination of Ash—Determination of Soluble and Insoluble Ash—Analysis of Ash of Vegetable-tanned Leathers—Determination of Epsom Salt—Analysis of Ash of Chrome-tanned Leathers—Determination of Nitrogen and Hide Substance—Determination of Fat—Determination of Matter Solu- ble in Water—Determination of Glucose—Determination of Min- eral Acid in Vegetable-tanned Leather—Determination of Sulfuric Acid and Neutral Sulfate in Chrome-tanned Leather—Determina- tion of Acidity (Basicity) of Chromium Salt—Determination of Hydrochloric Acid and Neutral Chloride in Chrome-tanned Leather —Determination of Combined Tannin—Compositions of Typical Leathers—Effect of Location on Composition—References.	
CHAPTER III	
MICROSCOPIC EXAMINATION OF SKIN AND LEATHER	65
Sampling—Dehydrating and Imbedding—The Microtome— Sharpening the Knife—Sectioning—Staining—Freezing Micro- tome—The Microscope—The Eyepiece—Micrometer Eyepieces— Compensating Eyepieces—Flat-field Eyepieces—Mechanical Stage—Binocular Wide-field Microscope—References.	
CHAPTER IV	
PHYSICAL PROPERTIES OF LEATHER	86
Strength and Stretch—Resistance to Tearing—Stitch Tear— Resistance of Grain to Cracking—Wear Resistance—Ventilating Properties—Water Absorption—Dimensional Changes with Rela- tive Humidity—Resistance to Heat—Resistance to Acids—Tem- perature Rise in Sunlight—Temper—Resilience—Break—Den- sity—Yield Values—References.	
CHAPTER V	
BACTERIAL COUNTS.	135
Bacteria—Bacterial Damage to Skins—Effect of pH Value—	

Making Bacterial Counts—American Public Health Association
Methods for Bacteriological Examination of Water—Examples—
Effect of Salts—Examination of Pure Cultures—References.

CHAPTER VI

MEASURING ENZYME ACTIVITY	153
Principles Involved: Choice of Substrate—Keratoses—Elastin— Collagen—Casein—Lipolytic Activity—References.	

CHAPTER VII

MEASURING pH VALUE	168
Methods of Expressing H-ion Concentration—Methods for Meas- uring pH Value (General)—Principle of the Hydrogen Electrode— Hydrogen Electrode Vessels for Tannery Liquors—Platinizing the Electrodes—Preparing the Calomel Electrode—Hydrogen Sup- ply—Assembly of Apparatus—Principle of the Potentiometer— Construction and Operation of Potentiometers—Recording Poten- tiometer—Carrying Out a Determination of pH—Calculation of pH from Voltage—Standardizing pH Measurements—Special Cases: Sources of Trouble—Quinhydrone Electrode—Glass Elec- trode—Indicator Method—Choice of Indicators—Preparing Indi- cator Solutions—Comparison Standards (Buffers)—Comparator— Other Forms of Permanent Standards—Hydrogen Ion Colori- meter—Use of the Colorimeter for Tannin Solutions—Highly Colored Solutions (Thompson-Atkin Method)—Potentiometric vs. Colorimetric Methods—Potentiometric Titrations—References.	

CHAPTER VIII

BEAMHOUSE MATERIALS AND LIQUORS	219
Curing Materials—Sodium Chloride (Common Salt)—Mercuric Chloride (Corrosive Sublimate)—Soak Liquors and Soaking Mate- rials—Water—Sodium Hypochlorite (Bleach)—Calcium Hypo- chlorite—Used Soak Liquors—Unhairing Materials and Lime Liquors—Lime—Sodium Sulfide—Barium Sulfide—Calcium Sul- fide or Sulfhydrate—Arsenic Sulfide—Sodium Hydroxide—Cal- cium Chloride—Used Lime Liquors—Bating and Deliming Mate- rials and Liquors—Ammonium Chloride—Ammonium Sulfate— Pancreatin—Mixed Dry Bates—Used Bate Liquors—Drenches— References.	

CHAPTER IX

VEGETABLE TANNING MATERIALS.	267
Methods of the American Leather Chemists Association: Samp- ling—Methods of the A.L.C.A.: Analysis—International Method (Provisional Method of the A.L.C.A.)—Comments of the Official Methods—Wilson-Kern Method—Other Methods for Tannin Determination—Identification of Tanning Materials—Specific	

Gravity—Ash—Sulfate—Chlorine—Glucose—pH Value—Total Acid in Tan Liquors—Color of Tanning Extracts—Plumping Power of Tan Liquors—Average Compositions of Typical Tanning Materials—Syntans—References.

CHAPTER X

CHROME TANNING MATERIALS AND LIQUORS	320
Chromium Sulfate—Chromium Chloride—One-bath Chrome Liquors—Sodium Dichromate—Aluminum Sulfate—Sulfuric Acid (Vitriol)—Hydrochloric (Muriatic) Acid—Pickle Liquors—Sodium Thiosulfate (Hypo)—Sulfites—Sodium Carbonate and Bicarbonate—Sodium Borate (Borax)—Sodium Phosphate—References.	

CHAPTER XI

FAT LIQUORING AND STUFFING MATERIALS AND LIQUORS.	352
Fixed, Non-drying Fats and Oils—Specific Gravity—Melting Point—Viscosity—Cloud Point and Pour Point—Water—Ash—Sediment (Matter Insoluble in Benzene)—Unsaponifiable Matter—Unoxidized and Oxidized Fatty Acids—Free Fatty Acids (Acid Number)—Iodine Value—Saponification Value (Koettsdorfer Number)—Hydroxyl (Acetyl) Value—Maumené (Thermal) Value—Analysis of Mineral Oil and Paraffin—Analysis of Moellon Dégras—Analysis of Sulfonated Oils—Separation of Sulfonated and Unsulfonated Oil—Analysis of Soap—Analysis of Egg Yolk—Analysis of Used Fat Liquors—References.	

CHAPTER XII

COLORING, FINISHING, AND MISCELLANEOUS MATERIALS.	416
Dyestuffs—Mordants and Strikers—Titanium Potassium Oxalate—Potassium Antimonyl Tartrate (Tartar Emetic)—Organic Acids—Formic Acid—Lactic Acid—Acetic Acid—Oxalic Acid—Ammonia—Finishing Materials—Casein—Egg Albumin. Blood Albumin—Waxes—Carnauba Wax—Shellac—Gums and Mucilages—Formaldehyde—Pigment Finishes—Linseed Oil—Vulcanized Oils (Viscols)—Nitrocellulose Finishes and Their Constituents—Nitrocellulose—Plasticizers—Solvents and Diluents—Mixed Lacquers—References.	

CHAPTER XIII

PREPARATION OF STANDARD SOLUTIONS	474
Acids and Alkalies—Silver Nitrate—Potassium Permanganate—Standard Solutions for Iodimetry—Indicators.	
AUTHOR INDEX.	483
SUBJECT INDEX.	489

ANALYSIS OF LEATHER

CHAPTER I

INTRODUCTION

Most of the materials involved in the manufacture of leather consist of substances of unknown or of extremely complex chemical composition, which are often present in systems of very complicated equilibria or in systems approaching but never reaching definite equilibrium. In order to get working ideas of the compositions of these materials, it has been found necessary to devise empirical methods. These methods, although designed to serve special purposes, may prove to be valuable guides in a practical way, if their limitations are well understood. On the other hand, they may be misleading to the point of absurdity in the hands of an analyst who does not understand the facts on which they were based. Many of the methods described in the following chapters are, of necessity, empirical. They should, therefore, be used with the utmost caution and only with a full understanding of their limitations, which the authors have tried to make clear.

Although protein-like substances have been synthesized, no one has yet succeeded in determining the molecular structure of any one of the proteins of the skin. In fact, it appears probable that the chemical compositions of the skin proteins vary with the kind of animal, its age, feeding, state of health, and experiences undergone during its life. In the manufacture of ordinary leathers, the tanner removes from the skin the hair, epidermis, sebaceous glands, fatty tissues, and soluble proteins, leaving a skin composed chiefly of white connective tissue made up of the class of proteins known collectively as collagen. The purest forms of collagen contain about 17.8 per cent of nitrogen. Since most of the materials used in tanning add very little nitrogen to the final product, it is possible to calculate the amount of collagen, or hide substance, present in the leather by multiplying its total nitrogen content by 5.62. But this simple method should not

be used blindly. If a leather is heavily impregnated with lacquer or with insoluble aniline dyestuffs, this method might prove very misleading. It is obviously not applicable to furs, which still contain the nitrogenous principles of the hair and epidermis.

A few tannins have been synthesized, notably pentadigalloyl glucose, but yet the compositions of practically all of the tannins in practical use are unknown. Fortunately, this is no handicap, because what the tanner wants to know is only how much of the tanning material will form a stable compound with the skin and what effect it has upon the properties and yield of leather. This permits the development of empirical methods of much greater value to the tanner than any absolute determination of tannin.

It seemed logical to shake hide substance with a solution of the tanning material until all tannin was removed from solution, as shown by qualitative tests, and then to measure the loss in concentration of material from the solution. Although this principle is the basis for practically all official methods used in the world for determining tannin, it fails to recognize that a large and variable fraction of the non-tanning material is removed from solution along with the tannin. A wide variety of results can be obtained by varying the concentration of tanning material in the solution, the proportion of hide substance to solution, time of shaking, temperature, acidity, etc. Since the various official methods are used chiefly to determine the selling price of tanning extracts, sold on a tannin basis, it was necessary, in order to insure concordance in the analyses of seller and buyer, to set definite limits of concentration, proportion of hide powder to solution, time of shaking, temperature, etc. A change in the value of any one of these purely arbitrary limits may produce a relatively large change in the apparent amount of tannin found by the method.

The analyst should be fully aware that these methods do not give the true tannin content of a material, nor even the amount of material that will form a stable compound with leather, but merely an arbitrary value upon which to base a selling price. Many unwary chemists have been led into serious error through the blind acceptance of an official method for a purpose other than that for which it was intended. The official methods of tannin analysis should not be used for any other purpose than price fixing without a thorough study of the facts and principles underlying them.

It is important, for some purposes, to know what proportion of leather is water soluble and what proportion can be leached out by water under certain conditions. As yet, chemists have not been able to agree upon a definition of water-soluble matter in leather that is determinable. In the various official methods, the so-called water-soluble matter is removed by washing the leather sample with water. But when leather is brought into contact with water, very complex equilibria are set up in which one substance may be divided among three phases: the free solution between the leather fibers, the solution absorbed by the leather fibers, and the insoluble structure of the fiber itself. If leather is extracted continuously with water, it will yield up something to the water as long as any leather is left. Methods have been worked out which have real significance and value, but they are not accepted for all purposes.

Even in the determination of the fat content of leather, involving extraction with an organic solvent, there is much disagreement due to the fact that each solvent seems to extract a different amount of material. The common official solvent is petroleum ether, but this does not extract oxidized fatty acids nor certain constituents of sulfonated oils, commonly used in fat liquoring leather.

These few examples serve to indicate the hopeless position of an analyst who does not understand the fundamental principles and facts underlying each method that he uses; he is almost certain to arrive at false conclusions when attempting to apply them to practical use. In the following chapters, the authors have attempted to guide the analyst in the selection of methods for his particular purposes. The methods of the American Leather Chemists Association are given along with methods which the authors have developed for use in a practical way. Before using any method given, the analyst should read all of the discussion in the chapter containing the method.

The chief purpose of chemical analysis in the tannery is to assist the tanner to produce, as economically as possible, leather of the highest attainable uniformity and excellence. In accomplishing this mission, the chemist is called upon to analyze the *product*, *i.e.*, leathers of various kinds at various stages of the process. He is also called upon to analyze the *raw materials*—vegetable tanning materials, chrome tanning compounds, fats, oils, soaps, and other fatty materials, and a host of accessories

ANALYSIS OF LEATHER

both inorganic and organic in chemical classification, that the tanner uses in producing leather. Finally, he must analyze *tannery liquors* of all sorts—soaks, limes, bates, pickles, chrome- or vegetable-tanning liquors, bleaches, fat liquors, color liquors, and finishes—to name only the more prominent examples.

It occasionally happens that leather is bought on specifications that include requirements as to its chemical composition. Much more often, however, leather is bought according to the buyer's judgment of a host of properties which determine the appearance of the leather, its wearing qualities in use, and its behavior in the hands of the buyer's workmen. Some of these properties are easily defined and described and easily tested. For example, leather of any kind must possess a minimum tensile strength. Other properties are extremely difficult to define and measure. The "feel" of shoe upper leather is a case in point. Methods for measuring certain of these properties are given in the following chapters, but the application of these tests is far from being the most valuable contribution that the chemist can make toward ensuring a uniformly good product. While he may not always be able to give a scientific explanation for the effects that he observes, the chemist, by analyzing leather after leather, recording his results in the form of graphic charts, and observing the changes in the properties of the leather that occur concomitantly with the elevations and depressions of his curves, can work out more or less definite optimum values for the composition of his leather. Perhaps it is more correct to say that he can work out more or less well-defined *limits* within which the composition of the leather may safely be allowed to vary without producing any appreciable change in the properties of interest to the buyer. He may find, for example, that when upper leather of a certain type contains less than a certain percentage of fat, the leather is underlubricated; that when the percentage of fat exceeds a certain value, the flanks and bellies are overlubricated. Similar connections, but often very far from being as direct as the one cited, will be found between degree of tannage, percentage of water-soluble matter, acidity, etc., and the several properties of the leather. Such connections cannot be established by making an analysis of 1 skin, or of 20 skins. It is only by analyzing hundreds of skins, recording the results graphically, and *noting trends* of the curves for degree of tannage or fat content or acidity that these relations can be discovered. This is a long and

expensive task, but the set of charts that results constitutes an extremely valuable "healthometer" for the operation of the tannery. Once normal values have been established for the different constituents of the leather, any decided departure from those values is a sign that some change has occurred in the process and that a corresponding change may be expected in the properties of the leather. It then becomes the chemist's business to find out what the change is (assuming the change to have been inadvertent) and see that the necessary steps are taken to bring the ship back to an even keel.

It may be added that such a set of charts will be of little use unless the chemist is able to judge the leather according to the buyer's visual and tactual tests, and unless the responsible operating staff appreciate the close connection that exists between the findings resulting from such tests and those resulting from the chemist's analysis of the leather.

Similarly, in analyzing and testing raw materials and liquors, the chemist's primary objective is to see that those materials and liquors have the same composition as similar materials that have previously given satisfactory results. Here, as in the case of leather analysis, the chemist must work out, for each constituent or variable property of each material and liquor, the limits within which variations may be permitted with safety. Here, again, the chart system is valuable, particularly for processes in which liquors are used repeatedly. The significant variables and the permissible limits of variation must generally be worked out by each chemist for his own particular set of plant operating conditions. The lime content of a used depilatory liquor might be extremely significant in a tannery in which only the quantity of lime which is necessary to saturate the solution initially is employed, while in a tannery operating with a large excess of lime present at all times it would hardly be worth determining. The sulfide content of a lime liquor is decidedly important. If the percentage of sulfide is too low, difficulty may be experienced in the mechanical unhairing; if too high, damage may be done to the skins; but both the upper and the lower limits depend upon such factors as duration and temperature of soaking and liming, type of skins, and even the mechanical condition of the machines used to scrape off the hair.

The determinations that should be made in analyzing a liquor or raw material are those which will tell whether or not that

material or liquor may safely be used in producing leather. The precision which should be striven for in carrying out the determinations depends upon the permissible latitude of variation of the quantity being determined. If it is known, for example, that the pH value of a given tan liquor must lie between the limits 4.5 and 5.5, it is obvious that the determination of pH value is one of the determinations required in order to tell whether or not the liquor is fit for use, and equally obvious that a precision of 0.05 to 0.10 pH unit is sufficient in obtaining the desired information. The analysis of any material is adequate when the determinations performed are sufficient, in nature and in precision, to detect any differences that may affect the quality of the stock between the material under examination and materials previously examined and found satisfactory in use.

The protection of the tanner against money loss due to possible fraudulent substitution of a cheaper for a more expensive material is quite secondary in importance to protecting him against the introduction into his tannery of materials different from those known to result in the production of satisfactory leather. When oils costing \$5 or \$10 are applied to a batch of leather potentially worth \$1,000, any possible direct loss due to substitution of a cheaper for a more expensive oil is insignificant compared to the losses that may result if the leather is spoiled or lowered in grade. The price-fixing aspect of the chemist's labors must not, of course, be neglected. A difference of 1 per cent in the tannin content of a carload of vegetable tanning extract may result in a price adjustment of several hundred dollars. It is not that such sums are not worth saving; it is rather that the chemist, in watching for such little leaks, should not lose sight of the greater opportunities for usefulness that are his in looking out for the hidden rocks and shoals.

CHAPTER II

CHEMICAL ANALYSIS OF SKIN AND LEATHER

It is so difficult to get a truly representative sample of raw skin that the sampling for analysis of large shipments as received at the tannery is impractical. The proportions of hair, adipose tissue, salt, water, etc., vary greatly from skin to skin in the same shipment and even in different parts of the same skin. Where skins have been improperly cured or fraudulent attempts have been made to increase their weight by adding loading materials, a qualitative examination of a few individual skins may be a valuable aid to the tanner in his purchasing, and such examinations are sometimes made. In order to place a quantitative value on an average shipment of skins, it is customary to use as a basis the quality and yield of the leather finally obtained from the shipment. While this method does not assist the tanner in the purchase of the particular shipment being tested, its continued use teaches him how, when, where, and from whom to purchase in order to get skins best suited to his needs.

The chemical analysis of skin and leather is of value to the tanner chiefly as a means of controlling his processes so as to produce the best possible leather at all times. In a tannery efficiently operated, periodic measurements are made of the chemical composition and physical properties of the finished leather. Standards are developed and analyses of skin, leather, and liquors at various stages of the process are valuable in helping to maintain them. Ordinarily, little is to be gained by sampling and analyzing the skins before they have been at least partially tanned.¹ Useful information may be gained by analyzing the skins after partial or complete tanning, after fat liquoring, coloring, stuffing, finishing, or any special operation.

When a protein is so altered in chemical composition as to become more resistant to hydrolysis, it is considered to have been

¹ Methods for the analysis of raw stock and of limed pelt have been published by Orthmann (64) and by Bennett (11).

- Numbers set in parentheses refer to References at end of chapter.

tanned and the material bringing about the change is called a tanning agent. In making leather, the protein used is the white connective tissue of animal skin, usually called collagen. Leather is collagen whose resistance to hydrolysis has been increased by the action of a tanning agent. In the commoner methods of tanning, this is brought about through the chemical combination of the collagen with the tanning agent. The two classes of tanning materials most widely used in making leather are the natural tannins, found in bark, wood, leaves, and certain fruits; and chromium salts. Other common tanning materials are salts of iron and aluminum, fish oils, formaldehyde, waste sulfite cellulose, and a number of synthetic organic compounds. Where a mineral salt has been used as the tanning agent, its amount is determined by analysis of the ash of the leather, but where an organic tanning agent has been used, its amount is determined by the difference between 100 per cent and the percentages of water, fat, protein, water-soluble material, ash of insoluble matter, and any other material known to be present and not included in the materials listed. Any water-insoluble organic matter other than fat or protein is thus usually included with organic tanning agent.

SAMPLING

Measurements of the chemical composition of leather are greatly complicated by the fact that it varies considerably over the area of the skin and also with increasing depth below the grain surface. Skins of the same kind, but of different thickness, will not have the same final composition, if kept together through all of the tannery processes, because many substances used in making leather are taken up by the skin in direct proportion to the surface area exposed and therefore will be found more abundantly in the thinner skins of a given lot and in the thinner parts of the same skin. Substances that diffuse into the skin slowly are usually found most abundantly in the outer layers, their amounts decreasing toward the middle layer of the leather. Methods of sampling leather for analysis must be modified according to the kind of leather and nature of the information desired.

Many attempts (15, 78) have been made to find places in the skin from which samples might be cut that represent the whole skin in average chemical composition without seriously damaging

the skin. Examples of these are given below in the methods of the American Leather Chemists Association. These methods are followed by one which the authors have long used for calf-skins at four stages of the process; a whole skin is destroyed each time, but the analysis covers the portion of the skin of greatest value to the consumer and upon which the sale value of the leather actually depends.

A. L. C. A. Method for Vegetable-tanned Leathers (2).—Take a cutting strictly according to the relative locations shown in Fig. 1 from each prescribed location of each piece sampled in any given lot of leather. Locations are given only relatively because of the variation in the size of hides and skins.

The double trims are not shown in the diagram. When sampling such trims, take cuttings from each prescribed location on each side of the backbone line. Whenever possible, take cuttings as prescribed for single bends, butts, and sides, as double bends, butts, and sides are much more difficult to sample satisfactorily. Each cutting is to be rectangular and 2 by 8 in. Take those from edge locations 0.5 in. in from the edge.

Prepare the entire cutting or cuttings from each location separately for analysis and, after thorough mixing, combine the same weight of leather from each location into a composite sample for analysis.

A. L. C. A. Method for Chrome-tanned Leathers (2).—Take cuttings strictly according to the relative locations shown in Fig. 2 (locations are given only relatively because of the variation in the size of hides and skins). Each cutting is to be half-moon shape, approximately 8 in. long by 2 in. at its greatest width. The straight edge of the cutting is to be taken 0.5 in. in from the edge of the piece sampled.

Take not more than one cutting from each piece when the lot consists of 12 pieces or more. With lots of less than 12 pieces, the number of cuttings from each piece sampled may be increased, provided that the same number of cuttings be taken from each piece sampled.

Authors' Method for Light Leathers.—In any average skin, the chemical composition is practically the same for all four strips indicated in the diagram in Fig. 3. The area covered by these strips is the really valuable portion of the leather and, therefore, the portion whose chemical composition

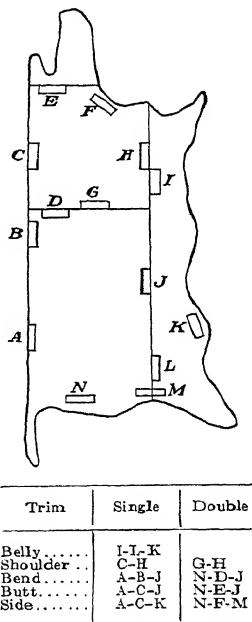
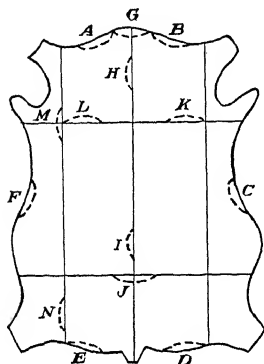


FIG. 1.—Showing location and size of cuttings to be taken in sampling vegetable-tanned leather for analysis by the methods of the American Leather Chemists Association.

is most important. The dimensions of each strip are 4 by 20 in.; a metal pattern is used to trace this area, which is then cut out with heavy shears.

When only the finished leather is to be analyzed, any one of the four locations may be taken. When the analyses



Trim	Locations
Whole skin.....	A-B-C-D-E-F
Side.....	A-F-E or B-C-D
Butt.....	D-E-J
Shoulder.....	G-K-L
Front.....	F-H-I
Belly.....	F-M-N

FIG. 2.—Showing location and size of cuttings to be taken in sampling chrome-tanned leather for analysis by the methods of the American Leather Chemists Association. Combine equal weights of leather from the same number of cuttings from each location into a composite sample for analysis.

are to be made in conjunction with the control of various processes, one strip may be cut after each of four processes. In this case, the entire pattern, slightly enlarged, is marked on the skin before the first sample is taken and then each sample is taken by cutting off the strip from head to tail of the skin, the exact cutting of 4 by 20 in. being made after the strip has dried. When periodic analyses are made, it is best to select skins of the same thickness so that variations due to thickness are not introduced to disturb the control.

In control work, it is often desirable to follow the changing composition of the leather from grain to flesh. In this case, the entire area of 16 by 20 in. is used. It is split into five or more layers on a band-knivesplitting machine and each layer is analyzed separately. For

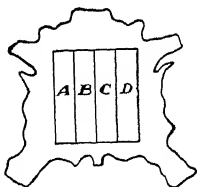


FIG. 3.—Showing location and size of cutting to be taken in sampling light leathers for analysis by the authors' methods. Any one of the four locations may be taken.

this purpose the authors now use a skiving machine such as is used in shoe factories; the Pluma type, model E,¹ makes a useful laboratory machine.

PREPARATION OF SAMPLE FOR ANALYSIS

Before the sample can be made sufficiently homogeneous to analyze properly, it must be reduced to a reasonably fine state of subdivision and thoroughly mixed. For heavy leathers, the conventional methods of disintegration are sawing and shaving with a sharp plane. In order to lighten the labor involved, several useful machines have been devised (8, 28, 63, 89). Clarke and Frey (20) examined four of these and concluded that either

¹ Made by United Shoe Machinery Co., Boston.

the Wiley mill or the Balderston slicer (8) is satisfactory in performance. The Wiley mill consists of six knives mounted in the inner periphery of a drum and four knives mounted on revolving arms which cut the leather to shreds by a scissors-like action. The Balderston slicer resembles an ordinary meat slicer. The end of the strip of leather is pressed against a revolving disk carrying a knife. Small blades mounted on the disk cut notches in the strip before each slice is cut, so that the product consists of tiny slices about 3 mm. long and 0.3 mm. thick. None of the machines so far proposed, excepting perhaps the Wiley mill, is adapted to cutting up leathers that do not possess considerable stiffness.

Light leathers are generally cut with shears, first into long strips about 2 mm. wide and then into squares. For cutting the long strips, the authors use a motor-driven photograph trimmer designed by Edwin A. Gallun. Any method of disintegrating the sample of leather that causes heating is undesirable because the composition of the leather may be considerably altered by the application of heat. For this reason, many chemists prefer cutting all samples into thin slices (42) and then cross-cutting.

A. L. C. A. Method (2).—Reduce the leather by cutting, planing, sawing, or other approved method to as fine a state of subdivision as is practicable, mix it thoroughly, place in a clean, dry container, and stopper tightly. Avoid heating the leather during its preparation. If the leather is prepared by sawing, take exceptional care in mixing to insure a uniform sample.

SPECIFIC GRAVITY

In correlating chemical analyses with physical properties of leather, it is often desirable to know the average thickness and apparent specific gravity of the leather. In the authors' method, the samples are cut exactly 4 by 20 in., the thickness is measured, with a gage reading accurately to 0.01 mm., in 30 places equally spaced, the measurements are averaged, and then the entire sample is weighed. The number of grams of leather per cubic centimeter of volume is taken as the apparent specific gravity. The sample is then cut up for analysis and bottled so as to permit the least possible change in water content before the analysis is started.

WATER

The commonest method for determining water is by loss in weight at a specified temperature in the neighborhood of 100°C.

Leather retains the last few per cent of water very tenaciously, and the higher the temperature employed in drying the higher will be the percentage of water found (87, 93), up to the temperature at which the leather begins to oxidize. A drying temperature of 95 to 100°C. is specified in the American Leather Chemists Association method. The authors believe that more consistent results can be obtained by drying at 100 to 105°C. This is the range recommended by a recent committee (42) of the International Union of Leather Industry Chemists. Dried leather is extremely hygroscopic, and great care must be taken to keep the dried samples from taking up water during cooling and weighing. The best method of doing so is to dry the leather in a wide and shallow glass-stoppered weighing bottle, with stopper removed, inserting the stopper the instant the sample is removed from the oven. If many samples are to be run, so that the supply of weighing bottles is inadequate, satisfactory results can be obtained by drying in an open dish, desiccating in an individual desiccator over fresh concentrated sulfuric acid, and transferring the sample rapidly to a weighed glass-stoppered bottle at the instant before weighing.

If the leather contains volatile substances other than water, the drying method gives results that are too high. This condition is apt to occur with leathers that have been heavily oiled with partially volatile mineral oils. For such leathers the toluene distillation method (3, 12, 45, 92), originally used for determining water in oils (23), should be employed. In this method water is expelled from the leather by treatment with boiling toluene and is caught and measured in a graduated trap. With a sufficiently large sample and a trap of small diameter, accurately calibrated, this method is probably more accurate than the drying method. As it is much more convenient to determine water by drying, the toluene distillation method is not widely used except where it is required by the presence of volatile oils.

Authors' Method.—Weigh accurately about 3 g. of leather into a wide-mouth, glass-stoppered weighing bottle, previously dried at 100 to 105°C., desiccated, and weighed. Place the bottle, with stopper removed, in an electrically regulated drying oven at 100 to 105°C. for 16 hr. Insert stopper, and place in an individual desiccator over strong sulfuric acid. Desiccate for 15 min. and weigh. Loss in weight is taken as water. If many samples are to be run, weigh each sample into a glass evaporating dish (not weighed), dry, and desiccate exactly 15 min. Transfer the sample

quickly, by means of glazed paper, to a tared glass-stoppered weighing bottle, and weigh.

$$\text{Per cent H}_2\text{O} = \frac{\text{g. loss in weight} \times 100}{\text{g. sample}}$$

Conduct each determination in duplicate. The dried residues may be used for determining ash or mineral acid in vegetable-tanned leather.

A. L. C. A. Method (2).—Place from 5 to 10 g. of the prepared leather in a weighing bottle or similar vessel that can be covered tightly. Dry for 16 hr. at 95 to 100°C., cover the container, cool in a desiccator, and weigh.

Toluene Distillation Method (3).—The apparatus (Fig. 4) consists of a 250-cc. round-bottomed flask connected by an angle tube carrying a graduated trap to a reflux condenser. The form manufactured and sold for determining water in oils may be used, but greater precision is attained by using a trap tube of smaller diameter, which can be made by sealing off a section from a 10-cc. Mohr pipette.

Clean the receiving tube and condenser tube with hot chromic acid, rinse successively with distilled water and 95-per cent alcohol, and dry them at 100°C. Assemble the apparatus as shown in Fig. 4. Weigh exactly 20 g. of leather and place in the distilling flask with about 100 cc. of toluene (b.p. 112°C.). Heat to boiling and distil at a rate such that about 2 drops of toluene fall from the tip of the condenser per second. When the water level in the trap is approximately constant, interrupt the distillation. Dislodge any drops in the condenser tube with a clean dry brush, saturated with toluene, inserting the brush through the top of the condenser and flooding the condenser with toluene. Dislodge any drops clinging to the side of the trap above the meniscus with a copper wire bent into a horizontal loop. Read the volume of water. Resume distillation. Repeat at intervals of about 30 min. until the water volume is constant. Calculate and report percentage of water.

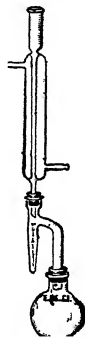


FIG. 4.—
Bidwell-
Sterling
apparatus
for
mination
of mois-
ture in
leather.

$$\text{Per cent H}_2\text{O} = \text{cc. H}_2\text{O} \times 5$$

If the trap is graduated in 0.1-cc. divisions capable of being read to the nearest 0.05 cc., the precision of the method is 0.25 per cent.

ASH

The mineral matter contained in leather is determined by ashing (70). The only precaution to be noted is that the temperature of ashing must not be higher than dull red heat (42), in order to avoid loss of chlorides. If the ash is to be analyzed, as is always the case with chrome leathers and frequently with vegetable leathers, a platinum dish should be employed. It is convenient to char the leather over a flame and complete the ignition in a muffle.

A. L. C. A. Method for Total Ash (2).—Ash from 5 to 15 g. of vegetable-tanned leather, or 3 g. of chrome-tanned leather, in a tared dish at a dull red heat. If it is difficult to burn off all the carbon, leach the residue with hot water, filter through an ashless filter, dry, and ignite the paper and residue, add the filtrate, evaporate to dryness, and weigh.

SOLUBLE AND INSOLUBLE ASH (77)

(Ash of Soluble and of Insoluble Matter)

The ash of the insoluble portion of the leather, generally called "insoluble ash,"¹ is determined after extracting the leather with water. The difference between total and insoluble ash is taken as soluble ash. The determination is a semiquantitative separation of alkali metal salts and of chlorides and sulfates of the alkaline earths from calcium carbonate, magnesia, and oxides of silicon, iron, aluminum, chromium, and other insoluble bases. The percentage of insoluble ash found is used in calculating fixed vegetable tannin.

The official method of the American Leather Chemists Association applies only to vegetable-tanned leather. In the A. L. C. A. method for water solubles, a 30-g. sample is employed, water solubles are determined by evaporation of a portion of the *extract*, and the extracted leather is dried at 60°C., after which a definite fraction of the material, or the entire sample, is taken for the determination of insoluble ash. The authors' method for determining water-soluble matter is different, and consequently their method for insoluble ash differs from the A. L. C. A. method in details. The authors use a smaller sample of leather for extraction and obtain the percentage of water solubles by drying the *residue of leather* at 100 to 105°C. and weighing. The entire sample is then taken for the ash determination.

A. L. C. A. Method for Insoluble Ash of Vegetable Leather (2).—Quantitatively remove the leather remaining after water extraction as described under Water Solubles—Extraction, dry it at a temperature not exceeding 60°C., and ash the entire charge or exactly one-half or one-third of it (equivalent respectively to 30, 15, or 10 g. of the original leather) as described under Total Ash. Cool in a desiccator, weigh, and express as percentage of the original leather.

¹ Accurately speaking, insoluble ash is that portion of the *total* ash which is insoluble. This is a very different quantity from insoluble mineral matter in the original leather (ash of insoluble matter), since, on ashing the leather, soluble mineral constituents may be rendered insoluble, and *vice versa*. The custom of referring to ash of insoluble matter as insoluble ash has, however, the sanction of universal usage and the advantage of brevity.

Authors' Method.—Ash the residue obtained in the determination of water-soluble matter by the Wilson-Kern method, as directed under total ash. Calculate and report percentage soluble and insoluble ash.

$$\text{Per cent insoluble ash} = \frac{\text{g. insoluble ash} \times 100}{\text{g. sample (weighed for detn. of fat)}}$$

$$\text{Per cent soluble ash} = \text{per cent total ash} - \text{per cent insoluble ash}$$

ANALYSIS OF ASH OF VEGETABLE LEATHERS

The ash of unfinished and uncolored, light vegetable leathers is generally small in quantity and consists mostly of lime, magnesia, and traces of iron and alumina. Finished leathers of this class have a somewhat larger ash but generally less than 1 per cent. They may contain considerable amounts of iron oxide, if pigment finishes have been used, and aluminum, antimony, and titanium derived from the mordanting baths. Heavy vegetable leathers often contain Epsom salt and may contain barium sulfate or other inert loading material.

The methods of the American Leather Chemists Association provide for the determination of magnesium sulfate only. The authors' procedure includes methods for the determination of silica, antimony, titanium, iron, aluminum, barium, calcium, and magnesium. It is very unlikely that all these substances will be found in any one leather, and considerable time may be saved by making qualitative tests when analyzing the ash of a leather of unknown composition. Sometimes these tests will give all the information needed. The complete analysis of the ash is hardly justified as a routine procedure, except when the percentage of ash is unusually high, but gives valuable information regarding abnormal or unfamiliar leathers.

Qualitative Test for Antimony.—Ash 2 or 3 g. of leather, dissolve the ash in about 10 cc. of concentrated hydrochloric acid, dilute with about 40 cc. of water, and heat to boiling. Pass hydrogen sulfide gas through the solution. A yellow precipitate, changing to orange, indicates the presence of antimony.

Qualitative Test for Titanium.—Ash 2 or 3 g. of leather and fuse the ash with potassium hydrogen sulfate. Dissolve the fusion in 5 per cent sulfuric acid and treat with about 5 cc. of 3-per cent hydrogen peroxide solution made by diluting pure concentrated perhydrol. An intense yellow color indicates the presence of titanium.

Qualitative Test for Barium Sulfate.—Ash about 1 g. of leather, fuse with sodium carbonate, and dissolve the fusion in hot water. If an insoluble residue is present, filter, wash with hot water until the filtrate is neutral, and dissolve the residue in dilute hydrochloric acid. Treat the hot solution

with a few drops of dilute sulfuric acid. A white precipitate indicates the presence of barium sulfate in the ash.

Silica (Titanium and Barium Absent).—Fuse the total ash in a platinum crucible with 2 or 3 g. of pure anhydrous sodium carbonate over a good Meker burner. Cool. Treat with about 50 cc. of water and 5 cc. of concentrated hydrochloric acid, cover, and let stand until the fusion is completely decomposed. Rinse the cover glass and transfer the solution to a small casserole. Evaporate to dryness on the hot plate, bake the residue at not over 120°C., and take up with about 10 cc. of concentrated hydrochloric acid. Let stand about 5 min. Dilute with water and filter at once through ashless paper. Wash free from chlorides. Ignite the paper and insoluble matter in a weighed platinum crucible, cool in a desiccator, and weigh. If more than traces of silica are present, treat the residue with 5 to 10 cc. of hydrofluoric acid and a few drops of concentrated sulfuric acid. Evaporate to dryness and ignite at bright red heat. Cool in a desiccator and reweigh. Take the difference in the two weights as silica. If the residue remaining after treatment with hydrofluoric acid exceeds 0.001 g., fuse it with a little sodium carbonate, dissolve the fusion in dilute hydrochloric acid, and add the solution to the filtrate from the silica.

$$\text{Per cent SiO}_2 = \frac{\text{g. SiO}_2 \times 100}{\text{g. leather ashed}}$$

For the procedure in the presence of titanium, see under Titanium. For the procedure in the presence of barium sulfate, see under Barium Sulfate.

Iron.—Dilute or concentrate the filtrate from silica to 100 to 150 cc. Add a few drops of methyl red indicator, and add ammonia drop by drop until the solution turns yellow. Heat to boiling and boil until the excess ammonia is expelled and the solution turns pink. Filter and wash several times with hot water.

If the amount of precipitate is small, and the separation of iron and aluminum is not desired, continue washing until the precipitate is free from chlorides, dry the paper and precipitate at about 100°C., and ignite to constant weight in a weighed crucible. Cool in a desiccator and weigh as aluminum oxide plus iron oxide.

If the amount of precipitate is considerable, place the paper and precipitate in the beaker used for the first precipitation, dissolve the hydroxides by adding a few cubic centimeters of concentrated hydrochloric acid, dilute to about 100 cc., macerate the filter paper, and reprecipitate the mixed hydroxides as before, in case the separation of iron and aluminum is not desired. Filter, wash free from chlorides, ignite, and weigh the mixed oxides.

If the separation of iron and aluminum is desired, dissolve the first precipitate by pouring concentrated hydrochloric acid on to the filter, and wash thoroughly, receiving the filtrate and washings in the beaker used for the first precipitation. Add pure solid sodium carbonate until the solution is slightly alkaline, then make slightly acid with hydrochloric acid. Add about 1 g. of sodium peroxide (free from iron and aluminum). Boil on the hot plate, or over a very small flame, for about 10 min. to decompose most of the peroxide (which otherwise will attack the filter), filter through ashless

filter paper, and wash about six times with hot water. Save the filtrate for the determination of aluminum. As it is very difficult to free the precipitate and paper from alkali, redissolve the precipitated iron hydroxide with hydrochloric acid, and reprecipitate with ammonia as above directed. Filter, wash clean, ignite, and weigh as iron oxide. Discard the filtrate from the final precipitation. Calculate and report percentage of iron as oxide.

$$\text{Per cent Fe}_2\text{O}_3 = \frac{\text{g. Fe}_2\text{O}_3 \times 100}{\text{g. leather weighed for ash determination}}$$

Aluminum.—Acidify the filtrate from the precipitation of iron hydroxide, and concentrate to 100 to 150 cc. Precipitate aluminum as hydroxide with ammonia as above directed, filter, wash clean, ignite, desiccate, and weigh as aluminum oxide. Calculate and report percentage of aluminum as oxide.

$$\text{Per cent Al}_2\text{O}_3 = \frac{\text{g. Al}_2\text{O}_3 \times 100}{\text{g. leather weighed for ash determination}}$$

NOTES.—Experiments performed by Henrich in the authors' laboratory indicate that this method of separating iron and aluminum is quite accurate if carried out according to the above directions. The results, calculated as percentages of the leather, are correct to within about ± 0.02 per cent.

Calcium.—Dilute or concentrate the combined filtrates from aluminum to about 400 cc. Heat to boiling. Add about 10 cc. of concentrated hydrochloric acid and 15 cc. of saturated oxalic acid solution or 10 cc. of 10-per cent ammonium oxalate solution. Let stand 5 min. Make slightly alkaline with ammonia. Allow the precipitated calcium oxalate to settle for at least 1 hr., preferably overnight. Filter through close-textured paper (Whatman No. 44 or its equivalent), and wash three times by decantation and three times on the filter with dilute ammonium hydroxide (1:10). Ignite in a tared crucible first over a small flame and finally over a Meker burner. Cool in a desiccator and weigh *quickly*. Repeat to constant weight. Calculate and report percentage of calcium oxide.

$$\text{Per cent CaO} = \frac{\text{g. CaO} \times 100}{\text{g. leather ashed}}$$

Magnesium.—Evaporate the filtrate from calcium to about 300 cc. Make slightly acid with hydrochloric acid, cool if necessary, and add 100 cc. of a 10-per cent solution of sodium ammonium hydrogen phosphate (microcosmic salt). While stirring vigorously, add to the solution dilute ammonium hydroxide (1:10) until the solution is just alkaline, let stand 15 min., and then make strongly alkaline with ammonia. Let the precipitate settle overnight.¹ Filter on a tared Gooch crucible, wash three times with dilute ammonium hydroxide (1:40), and ignite at the maximum temperature

¹ In the presence of more than traces of magnesium, the precipitate should always be redissolved in dilute hydrochloric acid and reprecipitated as above described.

of the Meker burner. Cool in a desiccator and weigh. Repeat to constant weight. Calculate and report percentage of magnesium oxide.

$$\text{Per cent MgO} = \frac{\text{g. Mg}_2\text{P}_2\text{O}_7 \times 36.21}{\text{g. leather ashed}}$$

Titanium.—If titanium is known to be present, or is found by qualitative test, bring the ash into solution with sodium carbonate and hydrochloric acid as usual, transfer the solution to a small casserole, evaporate nearly to dryness, and add 15 cc. of dilute sulfuric acid (1:1). Evaporate till copious fumes are evolved, then add 50 to 60 cc. of water and 5 to 10 cc. of hydrochloric acid. Filter and determine silica as directed under Silica. Regardless of the amount of silica found, volatilize it with hydrofluoric and sulfuric acids, being careful to expel all hydrofluoric acid. Fuse the non-volatile residue with a little potassium hydrogen sulfate, dissolve in dilute sulfuric acid, and add to the filtrate from the silica. To the combined solutions add a slight excess of ammonia, boil till the odor can scarcely be detected, filter the precipitated oxides of titanium, iron, and aluminum, and wash three times with hot water. Redissolve the precipitate in dilute hydrochloric acid, receiving the filtrate in the beaker used for the precipitation. Add concentrated ammonium hydroxide drop by drop till a very slight permanent precipitate forms, then add hydrochloric acid till the precipitate just redissolves. Dilute to 300 cc. Saturate the solution with sulfur dioxide, and boil until titanium is precipitated and the solution smells faintly of sulfur dioxide. Filter, wash the precipitate with hot water containing a little sulfurous acid, ignite in a tared crucible over a Meker burner, cool in a desiccator, and weigh as titanium oxide. Calculate and report percentage of titanium oxide.

$$\text{Per cent TiO}_2 = \frac{\text{g. TiO}_2 \times 100}{\text{g. leather ashed}}$$

Determine iron and aluminum in the filtrate from titanium, and calcium and magnesium in the combined filtrates from aluminum as described above.

Barium Sulfate.—Fuse the total ash with about 5 g. of pure anhydrous sodium carbonate over a good Meker burner. Cool. Dissolve the fusion in hot water, filter off the insoluble carbonates, and wash with hot water until the washings are no longer alkaline to phenolphthalein. Save the filtrate. Dissolve the insoluble carbonates from the filter with dilute hydrochloric acid and boil to remove carbon dioxide. To the hot solution add 10 cc. of dilute sulfuric acid drop by drop. Allow the precipitate to settle overnight. Filter through close-texture filter paper (Whatman No. 44 or its equivalent), and wash free from chlorides with hot water. Dry the precipitate at 100°C., and ignite in a tared crucible. Heat gently until the paper is completely charred then increase the temperature to the point where the carbonaceous matter ignites, and finally to the full heat of a good Bunsen burner.¹ Allow free access of air during the ignition. Cool in a desiccator and weigh. Calculate and report percentage of barium sulfate.

$$= \frac{\text{g. BaSO}_4 \times 100}{\text{g. leather ashed}}$$

¹ At the maximum temperature of a good Meker burner, there is danger of decomposing barium sulfate.

Combine the filtrate from barium sulfate with that from the insoluble carbonates and determine silica, aluminum, iron, calcium, and magnesium by the methods already given.

A. L. C. A. Method for Magnesium Sulfate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, in Vegetable Leather (2).—Ash 5 or 10 g. of prepared leather as directed under Total Ash. Carefully moisten the ash with water, add 15 ml. of concentrated hydrochloric acid, wash into a beaker, dilute to 50 to 75 ml., add 2 or 3 drops of concentrated nitric acid, and gently boil or heat on a steam bath for 15 min. Without filtering off insoluble matter, add ammonium hydroxide (1:1) slowly with stirring until nearly neutral, and then add dilute ammonium hydroxide in very slight excess. (If the precipitate does not have the characteristic reddish-brown color of ferric hydroxide and there is known to be present enough ammonium chloride to hold in solution all magnesium, redissolve in hydrochloric acid without filtering, add a few drops of pure ferric chloride solution, and reprecipitate with ammonium hydroxide.) Boil for a few minutes, filter, and wash the precipitate thoroughly with hot water. If necessary, evaporate the filtrate to 175 to 200 ml. and make ammoniacal (about 1 ml. of ammonium hydroxide), boil gently, and add slowly with constant stirring 10 ml. of a saturated solution of ammonium oxalate. Cover and let stand 2 hr. or longer on a steam bath or in a warm place. Quantitatively transfer solution and precipitate to a 250-ml. volumetric flask, cool to 20°C ., dilute to volume, and mix thoroughly. Filter through quantitative paper, making sure that the filtrate is clear. Pipette an aliquot equivalent to 2 g. of the original leather and dilute to about 150 ml. Make slightly acid to methyl orange with hydrochloric acid, cool if necessary, and add a slight excess of a clear saturated solution of sodium ammonium hydrogen phosphate (5 ml. generally sufficient). While stirring vigorously add a few drops of ammonium hydroxide until precipitation just starts or until faintly ammoniacal. Let stand 15 min., add with stirring 5 ml. of concentrated ammonium hydroxide, cover, and let stand overnight at room temperature. Determine the magnesium either by the gravimetric or the volumetric procedure.

Gravimetric Procedure.—Filter through a well-prepared Gooch, wash the precipitate free from chlorides with dilute ammonium hydroxide (1:9), and finally just moisten the precipitate with 2 or 3 drops of a solution of approximately 50 per cent ammonium nitrate in dilute ammonium hydroxide (1:9). Dry, ignite gently at first, cover the crucible, and ignite intensely for 20- to 30-min. intervals until the weight is constant. Weigh as magnesium pyrophosphate, multiply by 2.2135 to convert to magnesium sulfate heptahydrate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and express as percentage on 2 g. of leather.

Volumetric Procedure.—Filter clear, through close quantitative paper, and wash the precipitate free from chlorides with dilute ammonium hydroxide (1:9). Remove the ammonia wash water, by washing three to four times with neutral 60-per cent by volume methylalcohol solution, or by spreading the filter paper with its precipitate on coarse absorbent filter paper for a few minutes and then on a watch glass for 1 hr. at 50°C . (if 60°C . is exceeded, discard the determination), or by air-drying the opened filter with its precipitate overnight at laboratory temperature. After removal of the ammonia wash water, transfer the filter paper with its precipitate to a beaker or flask,

moisten with water, thoroughly disintegrate the paper, and add an accurately measured excess of tenth-normal sulfuric acid and 2 or 3 drops of 0.1-per cent solution of methyl orange. Dilute to about 100 ml. and determine the excess of acid by titrating with tenth-normal sodium hydroxide to a clear yellow without any suggestion of pink. One milliliter of tenth-normal sulfuric acid is equivalent to 0.0123 g. of hydrated magnesium sulfate. Express the result as percentage magnesium sulfate heptahydrate on 2 g. of leather.

ANALYSIS OF ASH OF CHROME-TANNED LEATHERS

(5, 6, 38, 39, 40, 51, 54, 62, 94, 101)

In mineral-tanned leathers, of which chrome leather is by far the most important, the tanning agent is determined by analysis of the ash. The ash of chrome leather consists predominantly of chromic oxide but generally contains some alumina and a little iron oxide, since these are present in most commercial chrome-tanning compounds. In addition, the ash may contain a little calcium and small amounts of sodium salts. Chrome sole leather ash may contain barium sulfate.

The methods of the American Leather Chemists Association provide for the determination of chromium, iron and aluminum (not separated), and barium sulfate. Experiments performed by Henrich in the authors' laboratory indicate that these methods are at fault in not specifying a double precipitation of iron and aluminum, to remove occluded chromium. The authors also believe it desirable to determine iron and aluminum separately. Their methods are given below, in addition to the A. L. C. A. methods.

Chromium is almost universally determined iodimetrically, after oxidizing to chromate by an alkaline oxidizing fusion. Wet oxidizing methods, employing either the leather or the solution obtained in determining hide substance, have been used but have little to recommend them. Wet oxidation of the leather is best effected by digestion with hot dilute hydrochloric acid, followed by treatment with sodium peroxide. It is difficult to decompose the proteins to such a point that the products have no reducing action, and the complete decomposition of the peroxide is troublesome. The method has no justification except when a large number of leathers must be analyzed quickly with an inadequate supply of platinum dishes. Determination of chromium in the nitrogen-determination residues is pointless unless the sample is extremely scanty. Oxidation in the dry way may be effected either by heating the ash with Eschka's mixture below the sinter-

ing point or by fusion with borax, sodium carbonate, and potassium carbonate. If Eschka's mixture is used, the ash must be thoroughly mixed with a large excess of the reagent by grinding, and the mass must be heated below the sintering point, with stirring by means of a platinum poker, until it attains a clear canary-yellow color. The borate-carbonate method is much simpler and gives equally good results. The authors have found that a mixture of 2 parts of soda to 1 of borax works just as well as the flux containing potassium carbonate specified in the official method. Incomplete decomposition and oxidation is shown by the presence of green particles insoluble in dilute acid when the fusion is dissolved. These must be filtered, ignited, and fused again. Iron must be removed before titrating the chromium, since iodine is liberated by ferric salts. The precipitated iron and aluminum hydroxides generally carry down some chromium, so that it is necessary to redissolve and reprecipitate the hydroxides, combining the second filtrate with the first. The titration of chromium is carried out by adding potassium iodide to a strongly acid solution, titrating the liberated iodine with standard sodium thiosulfate.

Authors' Method for Chromium, Iron, and Aluminum.—Fuse the ash of 3 g. of leather with about 4 g. of a mixture of 2 parts of powdered sodium carbonate and 1 part of powdered borax glass, free from iron and aluminum, in a platinum dish at bright red heat for about 30 min. Cool, submerge the dish in hot water in a beaker until the cake is loosened, remove the dish, and wash it thoroughly with dilute hydrochloric acid. Acidify the solution with hydrochloric acid, and test for barium by adding a few drops of sulfuric acid. If the solution is not clear, separate and determine barium as sulfate as prescribed in the methods of the American Leather Chemists Association given below.

Concentrate the solution, after the removal of barium if necessary, to about 100 to 150 cc. Add ammonia drop by drop until the solution is just alkaline, then boil until the excess ammonia is expelled. Filter the precipitated hydroxides of iron and aluminum, and wash several times with hot water. Set the filtrate aside. Dissolve the precipitate by pouring hydrochloric acid (1:1) over the filter, and wash thoroughly with hot water, receiving the solution in the beaker used for the first precipitation. Reprecipitate iron and aluminum as hydroxides with ammonia as above directed, filter, and wash thoroughly. Combine the first and second filtrates, and concentrate the solution to a volume of about 150 cc. Acidify with hydrochloric acid and add 10 cc. of concentrated hydrochloric acid in excess. Cool the solution to room temperature, add 10 cc. of a 15-per cent solution of potassium iodide, let stand for 2 min., and titrate the liberated iodine with recently standardized tenth-normal sodium thiosulfate. Add the thiosulfate until the brown color of iodine is nearly discharged, then add several cubic centi-

meters of starch indicator and continue adding thiosulfate, drop by drop, until the blue color changes to a clear sea green characteristic of trivalent chromium. Take the first disappearance of the blue as the end point, and ignore any return of color due to air oxidation. Calculate and report percentage of chromium as chromic oxide, Cr_2O_3 .

$$\text{Per cent} \quad \frac{\text{cc. } 0.1-N \times 0.2534}{\text{g. leather ashed}}$$

For methods of standardizing thiosulfate, see Chap. XIII. As thiosulfate is seldom exactly tenth-normal, a correction must of course be made before applying the above equation.

Redissolve the second precipitate of iron and aluminum hydroxides by pouring hydrochloric acid (1:1) over the filter, and wash the paper thoroughly with hot water. Make the solution slightly alkaline by adding pure solid sodium carbonate, then acidify with a few drops of hydrochloric acid. Add about 1 g. of sodium peroxide (free from iron and aluminum). This precipitates ferric hydroxide, while aluminum remains in solution. Boil on the hot plate, or over a very small flame, for about 10 min. to decompose most of the peroxide. Filter, and wash thoroughly with hot water. Save the filtrate for the determination of aluminum. As it is difficult to wash the iron hydroxide free from alkali, redissolve the precipitate with hydrochloric acid and reprecipitate with ammonia just as directed for the joint precipitation of aluminum and iron. Filter, wash clean, dry the paper at about 100°C ., and ignite to constant weight. Cool in a desiccator and Calculate and report percentage of iron as oxide.

$$\text{Per cent } \text{Fe}_2\text{O}_3 = \frac{\text{g. } \text{Fe}_2\text{O}_3 \times 100}{\text{g. leather ashed}}$$

Acidify the filtrate from the first (sodium peroxide) precipitation of iron, and precipitate aluminum as hydroxide with ammonia as above directed. Filter, wash, dry, ignite, desiccate, and weigh as oxide. Calculate and report percentage of aluminum as oxide.

$$\text{Per cent } \text{Al}_2\text{O}_3 = \frac{\text{g. } \times}{\text{g. leather ashed}}$$

A. L. C. A. Methods for Chromium, Barium, Iron, and Aluminum; *Fusion Mixture*.—Use a fusion mixture of equal parts of sodium carbonate, potassium carbonate, and powdered borax glass, free from impurities and particularly from compounds of chromium, barium, iron, and aluminum.

Determination.—To the ash from 3 g. of leather in a platinum crucible add 4 g. of the fusion mixture, mix well, fuse for 30 min., and let cool. Place the crucible in a beaker with enough hot water to cover it, and digest until the melt no longer adheres to the crucible. Remove the crucible, rinsing it thoroughly with hot water containing a few drops of concentrated hydrochloric acid. Cool the solution, acidify with hydrochloric acid, add 2 or 3 drops of sulfuric acid, and boil 2 min. If the solution is clear, proceed as directed under a.

If the solution is not clear, filter and wash the residue about three times with hot water. Reserve the filtrate and washings. Dry the filter and residue, ignite, fuse again, using about 1 g. of the fusion mixture, and treat the melt as after the first fusion. If the acidulated solution again is not clear, filter, wash the residue thoroughly with hot water, combine the filtrate and washings with those from the first fusion, and proceed as under *a*. Ignite the filter and residue, cool, weigh, and calculate as percentage barium sulfate.

a. To the clear solution add a very slight excess of ammonium hydroxide, boil about 2 min. and filter, collecting the filtrate in a 500-ml. volumetric flask. Wash the precipitate thoroughly with hot water, dry, ignite, cool, weigh, and calculate as percentage of oxides of iron and aluminum, ferric oxide plus aluminum oxide.

Cool the filtrate and washings in the 500-ml. flask to about 20°C., dilute to volume, and mix thoroughly. Pipette 100 ml. into a suitable flask, neutralize with concentrated hydrochloric acid, and add 5 ml. in excess. Also add 10 ml. of a 10-per cent solution of potassium iodide and titrate with tenth-normal sodium thiosulfate solution, using starch solution as indicator. Calculate the result as percentage of chromic oxide, Cr_2O_3 .

NITROGEN; HIDE SUBSTANCE (COLLAGEN)

The determination of hide substance is probably the most important in the entire analysis of leather. In comparing different leathers, it is necessary to calculate each significant constituent in terms of grams per 100 g. of hide substance. An error in the determination of hide substance creates an equal error in the percentage of fixed tannin found by difference, and, upon dividing by the percentage of hide substance found, the error is approximately doubled. The percentage of hide substance is obtained by determining nitrogen and multiplying by the factor 5.62. The accurate determination of nitrogen is not difficult, but every precaution must be taken to make the determination as exact as possible, since any error in the determination is multiplied nearly sixfold in the final calculation.

Nitrogen is determined by the familiar Gunning modification of Kjeldahl's method, in which the leather is digested with sulfuric acid and potassium sulfate, the ammonia formed liberated with sodium hydroxide and distilled into an excess of standard acid, the excess being back titrated with standard alkali. Certain catalysts hasten the digestion. Frey, Jenkins, and Joslin (30) have investigated the use of copper sulfate, mercuric chloride, and potassium perchlorate. They obtained the same result with each of these catalysts and with no catalyst, but each catalyst shortened the digestion period by about 3 hr. and rendered

complete digestion more certain of attainment. They recommend the use of copper sulfate, which is the cheapest of the three. The authors have employed copper sulfate with satisfactory results, thereby cutting the digestion period from 5 to 2 hr.

Certain details of the method are purely a matter of personal choice (9). It has been shown that sodium sulfate may be substituted for the more expensive potassium salt (48). The

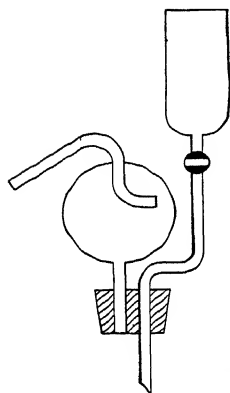


FIG. 5.—Distilling sodium hy-
droxide funnel for
Kjeldahl nitrogen
determination.

A. L. C. A. method prescribes a sample of 1.5 g., half-normal acid, and cochineal indicator. The authors prefer a 0.5 g. sample, tenth-normal acid, and methyl red. The percentage error is increased by the smaller sample but decreased by the use of the weaker acid. The larger sample is an advantage if the sample is not homogeneous, but the authors have experienced no difficulty in securing satisfactory checks with all kinds of leathers, properly prepared, using 0.5 g. Comparison of cochineal, methyl red, and cresol green indicators has shown that all three yield identical results (9). The boric acid method (26, 73), in which the ammonia is distilled into boric acid and titrated directly with methyl orange indicator, gives the same nitrogen percentages as the tenth-

normal acid absorption method and saves some time.

Instead of following the time-honored custom of pouring the strong alkali down the sides of the flask and subsequently connecting the flask with the distilling head, the authors introduce the alkali through a stopcock funnel, as shown in Fig. 5. The stem of the connecting bulb is cut off flush with the stopper, to eliminate a dead air space in which ammonia may be trapped. The absorbing solution (tenth-normal sulfuric acid or boric acid) is placed in a Volhard nitrogen bulb with enough water to seal the outlet to the side bulbs. A boiling chip such as a piece of clay pipe should be placed in the flask before stoppering.

A blank should always be run on each batch of acid and potassium sulfate. Usually the specified quantities of the reagents will contain volatile alkali equivalent to about 0.3 to 0.5 cc. of tenth-normal acid, which must be subtracted from the volume of acid consumed by ammonia liberated from the sample.

The factor for converting nitrogen to collagen was found by analysis of the purest obtainable hide substance. Kelly (46) reinvestigated the composition of pure collagen, obtained factors varying from 5.57 to 5.62, and recommends that the second decimal figure be dropped. The factor undoubtedly is different for different kinds of skin. If tenth-normal solutions are used, the calculation of percentage of hide substance is as follows:

$$\begin{aligned} &\text{Per cent hide substance} \\ &= \frac{(\text{cc. } 0.1\text{-}N \text{ H}_2\text{SO}_4 - \text{blank} - \text{cc. } 0.1\text{-}N \text{ NaOH}) \times 0.787}{\text{g. sample}} \end{aligned}$$

A. L. C. A. Methods for Nitrogen and Hide Substance (2). *Standard Acid.*—For ordinary purposes, half-normal acid is recommended. For determining very small quantities of nitrogen tenth-normal acid is recommended. Determine accurately the strength of the standard acid, either hydrochloric or sulfuric.

Standard Alkali.—A tenth-normal solution is recommended. Determine accurately its strength relative to the standard acid.

Concentrated Sulfuric Acid.—Use sulfuric acid of specific gravity 1.84 and free from nitrates and ammonium sulfate.

Sodium Hydroxide Solution.—Use a solution made in the proportion of 450 g. of sodium hydroxide, free from nitrates, dissolved in 1 l. of water.

Cochineal Solution.—Digest, with frequent shaking, 3 g. of pulverized cochineal in a solution of 50 ml. of strong alcohol and 200 ml. of water at ordinary temperature for from 1 to 2 days and filter. Use the filtrate as indicator.

Blank Test on Reagents.—Previous to use, test all reagents by a blank determination with sugar, which will partially reduce any nitrates present that might otherwise escape notice.

Determination.—Place 1.5 g. of prepared leather in a digestion flask, add 10 g. of pulverized anhydrous sodium sulfate and 25 ml. of concentrated sulfuric acid. Place the flask in an inclined position and heat below the boiling point until frothing ceases (a small piece of paraffin may be added to prevent extreme foaming). Then increase the heat and boil briskly until the liquid is quite clear and nearly colorless, usually in from 3 to 5 hr. (Do not let the bare flame touch the sides of the flask above the level of the solution at any time during the digestion.) Cool, dilute with about 200 ml. of water, and add enough sodium hydroxide solution to make the solution strongly alkaline, pouring it down the side of the flask so that it does not mix at once. Immediately connect the flask to a bulb trap and a condenser, mix its contents by shaking, and distill until all ammonia has passed over into a measured quantity of the standard acid. The distillation usually requires from 40 to 90 min. and the first 150 ml. will generally contain all of the ammonia. Titrate the distillate with the standard alkali solution, using cochineal as indicator. Calculate the percentage of nitrogen. Each milliliter of tenth-normal acid equals 1.4 mg. of nitrogen.

Boric Acid Method. *Boric Acid Solution.*—Dissolve boric acid free from borax, in the proportion of 45 g. per liter of water.

Methyl Orange Solution.—Dissolve methyl orange in the proportion of 0.1 g. per 100 ml. of water.

Determination.—Proceed as directed under Nitrogen, Kjeldahl Method, except distill the ammonia into about 125 ml. of the boric acid solution (roughly measured), and titrate the distillate with the standard acid solution, using methyl orange as indicator. Match the color of the end point of the boric acid blank and correct for the latter. Calculate the percentage of nitrogen.

Hide Substance.—The percentage of nitrogen multiplied by 5.62 gives the percentage of hide substance.

FAT

Much of the fat of raw skin is contained in the adipose tissue, which is removed in fleshing. After the removal of flesh, hair, and epidermal matters, cowhide or calfskin may contain less than 1 per cent of fatty material, while other kinds of skin, notably sheep, may contain very much more. Such skins are often degreased before tanning or coloring. After any skins have been tanned, it is necessary to treat them with fats, oils, or other materials to increase their suppleness and to modify their properties in other respects. These materials are added in the processes of fat liquoring or stuffing, oiling, and finishing (95). The kinds and amounts used differ greatly according to the kind of leather being treated. The materials most commonly used are (1) oils and fats, such as neat's-foot oil, olive oil, cod liver oil, and beef tallow; (2) sulfonated oils, particularly neat's-foot, cod, and castor; (3) vulcanized oils; (4) hydrocarbons, such as paraffin and mineral oils; (5) moellon *dégras*, an oxidation product of fish oils obtained as a by-product in the manufacture of chamois leather; (6) egg yolk; (7) waxes; (8) resins; and (9) soaps. When extracted from leather in making an analysis, all of these materials are included as fat.

The "fat" is extracted from a sample of leather by means of a suitable solvent and weighed after evaporating off the solvent. Because of the great variety of materials included in the determination, it is natural to find a variety of opinion as to the best solvent to use (1, 7, 22, 24, 42, 50, 82, 88, 91, 97, 98, 100, 102). The official method of the A. L. C. A. (2) specifies petroleum ether, which is not a good solvent for all materials added to leather in stuffing or fat liquoring. Over a decade ago, a committee of this association made a very thorough comparison of the relative efficiency of petroleic ether, carbon disulfide, carbon tetrachloride, ethyl ether, and chloroform (97). Whole skins of different

tannages were cut into sides before fat liquoring or stuffing, one side of each was stuffed or fat liquored, the material employed depending upon the type of leather, and then both sides of each skin were cut up, and samples of each extracted with each of the five solvents by each member of the committee. A condensed summary of the two thousand or more individual determinations is given in Table 1. There is comparatively little difference in the quantities of material extracted from leather by the different solvents before the oil treatment, but a very marked difference in the quantities extracted from the leather after treatment with fat. In every case chloroform extracted the most and petrolic ether the least. The percentage extracted by each solvent before fat liquoring was subtracted from the percentage extracted by the same solvent after fat liquoring. The solvent removing the most added fat (chloroform in every case) was given a "solvent efficiency" of 100, and the other solvents were assigned efficiencies in proportion to the quantities of added fat that they removed. These solvent efficiencies are given in Table 2. In every case petrolic ether has the lowest solvent efficiency of the five solvents. Taking chloroform as 100, the efficiency of petrolic ether varies from 96.6 to 64.6, depending upon the kind of fat present. The highest efficiency was shown when the leather contained stearin and paraffin, and the lowest when the leather contained sulfonated or oxidized oil. This is not surprising when it is recalled that the accepted method (2) for determining oxidized fat in mutton *dégras* depends upon its insolubility in petrolic ether. In consequence of failure to remove all the added fat, the apparent percentage of vegetable tannin in the leather increased during fat liquoring when petrolic ether was used as solvent. When the analysis was conducted with chloroform, the percentage of tannin remained constant, which of course it should do. This is shown in Table 3.

Objections were raised to the use of chloroform (1, 7, 53) because it dissolves some substances which are not fat, including small amounts of vegetable tannin (as shown by qualitative tests on the extracted material), some chromium (presumably present as chromium soap), and certain materials used in finishing, such as shellac and egg albumin. As far as tannin and chromium are concerned, the maximum error that can be introduced by using chloroform is the difference between the chloroform and petrolic ether extract from unfatliquored leather, which, as shown in Table

1, is never more than 0.5 per cent. The true error is much less, because chloroform is a much better solvent for cholesterol than is petrol, and natural leather fat is rich in this substance. Moreover, it is questionable whether the small amounts of chromium or vegetable tannin removed by chloroform were present in combination with collagen. So far as shellac and other finishing materials are concerned, while they are not fats, still less are they vegetable tannins, and it is as vegetable tannins that they are counted if not removed with fat, since vegetable tannin is determined by difference. In any case, the quantity of finishing materials applied to a skin is insignificant. For these reasons the authors have adopted and recommend the use of chloroform for the determination of fat in leather. Needless to say, the A. L. C. A. method must be used when leather is analyzed to determine whether it complies with government or other specifications where the A. L. C. A. method may be mandatory. In reporting the results of analysis, the solvent employed for fat should always be stated.

Authors' Method.—Weigh accurately from 5 to 8 g. of leather, place in an extraction thimble, plug the thimble with fat-free cotton, and extract with chloroform in a Soxhlet apparatus for about 8 hr. The top of the thimble must stand higher than the siphon, the chloroform must siphon off about every 15 min., and the quantity of chloroform taken should be about twice that required to fill the Soxhlet tube to the top of the siphon. Filter the extract through rapid filter paper into a weighed glass dish, or a weighed flask if it is desired to recover the chloroform. Rinse the extraction flask three times with chloroform, pouring the rinsings through the filter. Allow the chloroform to evaporate at room temperature (time is saved by using an electric fan) or distill from a water bath. Place the dish or flask in an oven at 100 to 105°C. for exactly 30 min. Place in a desiccator for exactly 15 min. and weigh. Replace in the oven for 15 min., desiccate, and reweigh. Repeat till the loss in weight on heating 15 min. is not more than 0.005 g. Calculate and report "percentage of fat (solvent: chloroform)."

$$\text{Per cent fat (solvent: CHCl}_3\text{)} = \frac{\text{g. residue} \times 100}{\text{g. leather}}$$

Preserve the extracted leather for the determination of water-soluble matter.

A. L. C. A. Method for Petroleum Ether Extract (2).—Extract from 5 to 30 g. of prepared leather in a Soxhlet or Johnson type of extractor with petroleum ether boiling between 50 and 80°C. until free from petroleum-ether extractive matter. Evaporate the ether and dry the residue at not more than 100°C. until it is approximately constant in weight. Avoid prolonged heating and possible loss of volatile constituents.

CHEMICAL ANALYSIS OF SKIN AND LEATHER

TABLE 1.—EXTRACTION OF FAT FROM LEATHER WITH DIFFERENT SOLVENTS

Kind of leather	Sampled	Grams extracted from 100 g. dry leather by				
		Petroleum ether	CS ₂	CCl ₄	(C ₂ H ₅) ₂ O	CHCl ₃
Vegetable kip.....	Before fat liquoring	0.36	0.44	0.50	0.84	0.68
	After fat liquoring with moellon <i>dégras</i>	11.15	11.93	12.55	13.34	13.29
	Apparent gain in fat	10.79	11.49	12.05	11.54	12.61
Black chrome calf.....	After blacking, before fat liquoring	1.13	1.34	1.57	1.44	1.63
	After fat liquoring with neat's-foot oil and soap	7.19	7.53	7.95	7.64	8.16
	Apparent gain in fat	6.06	6.19	6.38	6.20	6.53
Combination cowhide (army retan upper).....	Before stuffing	0.37	0.48	0.59	0.59	0.71
	After stuffing with stearin, paraffin, and wool grease	32.19	32.80	32.92	33.37	33.54
	Apparent gain in fat	31.82	32.32	32.33	32.78	32.83
Vegetable cowhide.....	Before fat liquoring and stuffing	0.29	0.35	0.42	0.56	0.66
	After fat liquoring with sod oil and stuffing with stearin	10.62	11.46	11.67	12.40	12.48
	Apparent gain in fat	10.33	11.11	11.25	11.84	11.82
Chrome kip.....	Before fat liquoring	0.54	0.72	0.83	0.77	0.94
	After fat liquoring with sulfonated neat's-foot oil	4.75	5.91	6.97	6.01	7.45
	Apparent gain in fat	4.21	5.19	6.14	5.24	6.51
Combination kip.....	Before fat liquoring	0.55	0.68	0.77	0.88	0.90
	After fat liquoring with sod oil and soap and stuffing with stearin	26.50	27.07	27.29	27.94	28.06
	Apparent gain in fat	25.95	26.39	26.52	27.06	27.16
Sole leather.....	After finishing	3.35	3.62	3.85	4.37	4.37
Sole leather.....	After finishing	2.47	2.66	2.70	3.22	3.33
Chrome retan upper.....	After finishing	17.80	18.13	18.12	18.15	18.45

TABLE 2.—RELATIVE EFFICIENCY OF DIFFERENT SOLVENTS FOR ADDED FAT IN LEATHER

Kind of leather	Fat liquored or stuffed with	Efficiency of solvent ($\text{CHCl}_3 = 100$)				
		Petrolie ether	CS_2	CCl_4	$(\text{C}_2\text{H}_5)_2\text{O}$	CHCl_3
Vegetable kip.....	Moellon <i>dégra</i> s	85.3	91.0	93.8	93.3	100.0
Black chrome calf.....	Neat's-foot oil and soap	92.4	94.6	97.5	94.9	100.0
Combination cowhide.....	Stearin, paraffin, and wool grease	96.6	98.2	98.4	99.7	100.0
Vegetable cowhide.....	Sod oil, soap, and stearin	87.1	93.7	94.9	100.0	100.0
Chrome kip.....	Sulfonated neat's-foot oil	64.6	79.7	94.3	80.7	100.0
Combination kip.....	Sod oil, soap, stearin	95.2	96.9	97.5	99.6	100.0

TABLE 3.—APPARENT CHANGES IN DEGREE OF TANNAGE DUE TO INCOMPLETE EXTRACTION OF FAT BY PETROL

Kind of leather	Apparent grams vegetable tannin per 100 g. collagen				
	Fat extracted with petroleic ether		Fat extracted with chloroform		
	Before fat liquoring	After fat liquoring	Difference	Before fat liquoring	After fat liquoring
Vegetable kip.....	59.48	62.60	+3.12	58.30	58.49
Vegetable cowhide.....	55.18	57.62	+2.44	54.91	54.81
					+0.19
					-0.10

When necessary, as later prescribed under Water Extract, and if desired, make the petroleum-ether extraction upon the 30-g. charge previous to water extraction.

Examination of Fat.—The fat extracted from leather may be examined by any of the methods given in Chap. XI. If a complete analysis is desired, enough leather should be extracted to give at least 5 g. of fat. The determinations of most value include (1) unsaponifiable matter; (2) unoxidized and oxidized fatty acids; (3) iodine value of the unoxidized fatty acids; (4) melting point of the unoxidized acids; and (5) sulfates combined with the oil, if the presence of sulfonated oil is suspected.

MATTER SOLUBLE IN WATER

Very divergent views are held as to the definition of water-soluble matter in leather and the proper method of determining it. Leather contains substances that are extracted by water at very different rates (55). These include (1) substances not combined with hide substance at all, such as soluble inorganic salts and organic compounds of low molecular weight, of which glucose may serve as an example; (2) substances more or less loosely combined with hide substance, including the so-called "non-tans" of natural tanning extracts; and (3) true tannins, that is, substances capable of precipitating gelatin. The uncombined matter is removed completely by extraction with water for about 2 hr. (55). The loosely combined matter is extracted by continuous percolation in about 4 days. At the end of this time the extract no longer gives the extremely sensitive ferric chloride test for soluble non-tans. True tannin forms a compound with hide substance that is hydrolyzed very slowly but still quite measurably. Merrill (55) and also Page (65) have found that no end point in the extraction of vegetable leather by water can be reached, and this is entirely in accordance with theory, since collagen tannate must possess a hydrolysis constant, though it happens to be a very small one. The rate of removal of tannin from leather depends partly upon how heavily the leather is tanned. Apparently hide substance combines very tenaciously with the first tannin taken up and less tenaciously with an additional quantity. The hydrolysis constant seemingly varies with different kinds of tannin, as might be expected.

It is not possible to remove all the uncombined soluble matter without extracting a large (and variable) fraction of the loosely

combined material or to extract all the loosely combined substances without dissolving some tannin. This makes the determination of water-soluble matter in leather an arbitrary one at best. However, if vegetable leather is extracted with water for several days, a point is reached where further extraction results in the removal of quantities of material so small that they can be detected only by extracting the leather for several days or weeks more. This point corresponds to complete removal of uncombined and loosely combined substances, plus a small amount of combined tannin. In the Wilson-Kern (96) method, the leather is extracted to this point. The end point is determined by failure of the extract to give a positive test for non-tannin with ferric chloride. The results obtained are reproducible and definite. Page (65) extracted leather with 20 to 25 l. of water, flowing at the rate of about 600 cc. per hour, and obtained constant results, practically identical with those yielded by the Wilson-Kern (96) method.

Table 4 shows the per cent of water-soluble matter, found by the Wilson-Kern Method, in vegetable-tanned calf skin that had not been colored or stuffed, using periods of extraction of from 1 to 112 days. The ferric chloride test was negative on the fourth day. While no absolute end point was reached, it will be seen that washing for 3 days beyond the end point caused an increase of only 0.76 in the percentage of water solubles found, while washing for 108 days after the end point caused an increase of only 5.33 per cent.

TABLE 4.—WATER-SOLUBLE MATTER AND TIME OF WASHING
(Vegetable-tanned Calf, After Tanning, Before Fat Liqueuring)

Days washed	Percentage of water-soluble matter found by Wilson- Kern procedure
1	13.90
2	16.03
4	20.45*
7	21.21
10	22.85
14	23.89
21	23.80
35	24.07
56	25.51
112	25.78

* Ferric chloride test on percolate negative; end point according to regular Wilson-Kern procedure.

Extraction with a small quantity of water, or for a short time, gives results that are entirely meaningless. During early stages of extraction, the curve for material removed as a function of time is very steep and is devoid of breaks of any kind. A method for determining water-soluble matter employing an extraction period of a few hours, or a volume of 2 l., as in the American Leather Chemists Association method, is not only purely arbitrary but also subject to great variation. The quantity of material reported as water-soluble according to this method includes all the uncombined soluble materials in the leather, plus a purely arbitrary and extremely variable fraction of the loosely combined substances. The only value that an empirical method such as this can possess is in affording a rough comparison between leathers of the same type, and then only if the arbitrary directions for making the determination are followed religiously.

One source of confusion in the evolution of a satisfactory method for determining water-soluble matter is a divergence of opinion as to the purpose of the determination (29, 58, 75, 81, 90, 96). Users of sole leather are interested in the "loading" which the leather has undergone—that is, in the quantity of material (glucose, Epsom salt, tannin, or non-tannin) deposited in the leather by impregnating it with a strong solution and drying out or in the quantity of material that will be leached out of the soles in actual wear. Upper leather manufacturers are more interested in the ratio of fixed tannin to the true water-soluble matter in their product, since this ratio, and also each of the two quantities individually, has a profound influence upon the properties of the leather and its behavior in several tannery operations. The A. L. C. A. method was designed primarily for heavy leather but probably gives results that are much higher than the loading factor or the material washed out in service. Page (65) has proposed a method for determining soluble loading materials, which is supported by convincing data. He digested 10 g. of leather with 100 cc. of water until equilibrium was attained (8 hr). An aliquot of the solution was evaporated and the residue weighed. The total soluble matter in the solution was calculated and found to check very closely with the weight of soluble matter in the tan liquor absorbed in the leather when it came out of the last layer.

In the A. L. C. A. method (2) for water solubles (applied to vegetable leather only), a charge of 30 g. is digested overnight

with water, and then extracted at 50°C. at such a rate as to give 2 l. of extract in 3 hr. Many different forms of extractors are in use (10, 60, 68), of which the one described by Reed and Churchill (68) (Fig. 6) is perhaps the most convenient. The sample is placed in the tube between two cotton plugs, the pinchcock is closed, and the tube filled about three-fourths full of distilled water. After standing overnight, the tube is closed with a one-hole rubber stopper and immersed completely in a tin-lined reservoir of distilled water maintained at 50°C. The

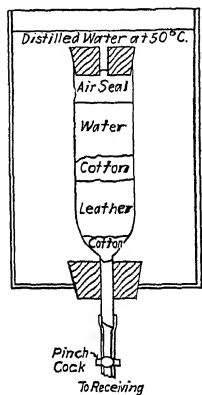


FIG. 6.—Reed and Churchill percolator.

pinchcock is opened, allowing the water in contact with the leather to drain slowly into the receiving flask, while water from the reservoir enters at the same rate. The air seal prevents the solution in the tube from mixing with the water in the reservoir. The rate of flow is so adjusted that 2 l. are collected in 3 hr.

A. L. C. A. Method for Water Solubles in Vegetable Leather. *Extraction.*—Digest 30 g. of prepared leather in a percolator overnight with sufficient water at laboratory temperature to cover the charge completely. Then extract at 50°C. with water at 50°C. at such a rate as to give 2 l. of extract in 3 h. Cool the extract to 20°C., dilute to volume, and reserve for the determination of soluble solids, non-tannins, and glucose.

If the leather contains on the moisture-free basis more than 8 per cent petroleum ether extract, extract the charge for water extraction first with petroleum ether boiling between 50 and 80°C., and let the ether evaporate spontaneously from the leather before proceeding with the water extraction.

Soluble Solids.—If the water extract is clear, pipette the 100 ml., evaporate, dry, and weigh as directed under Analysis of Tannin Extract Solution (Chapter IX).

If the water extract is not clear, proceed as directed under Analysis of Tannin Extract Solution.—Soluble Solids.

Express the result as percentage of the original leather.

Non-tannins.—Determine as directed under Analysis of Tannin Extract Solution.—Non-tannins, and express the result as percentage of the original leather.

Uncombined Tannin.—The difference between the percentage of soluble solids and the percentage of non-tannins is the percentage of uncombined tannin.

Wilson-Kern Method for Water Solubles in Leather.—Remove chloroform from the leather used for determining fat either by spreading out the sample on a watch glass and exposing to the air for 24 hr. or by heating

the extraction thimble in an oven at not higher than 50°C. for 8 hr. Transfer the sample to a Wilson-Kern extractor (Fig. 7) (56). Fasten a piece of muslin or filter cloth over the lower end of *B* by means of a rubber band held in place by the flange. Connect *C* and *B*, using a very thin film of vaseline to make a perfectly tight joint and eliminate danger of "freezing." Close the stopcock in *C*, and fill *B* half full of distilled water. Connect *B* and *A*, by means of a vaselined glass joint, close the stopcock in *A*, open that in *C*, and allow the water to run out until stopped by the lowered pressure inside the apparatus. Connect *A* to a reservoir of distilled water. Open the stopcock in *A*, and regulate the flow so that water drips from the outlet at a rate of about 20 drops per minute. Extract for about 24 hr.

Close both stopcocks and allow the leather to stand in contact with the water in the apparatus for 1 hr. Detach *B* from *A*. Open the stopcock in *C* and draw off the water in the apparatus, discarding the first 25 cc. To 10 cc. of the solution in a test tube add 1 drop of a 1-per cent solution of ferric chloride. If the color produced is a very light yellow or brown, free from any tint of blue or green, consider the extraction to be complete. If a green or blue tint is produced, resume washing, and wash for 24 hr. longer. Repeat until the ferric chloride test is negative.

In the case of chrome-tanned leathers that have not been vegetable retanned, wash for 24 hr.

Allow the extractor to drain. Transfer the sample quantitatively to a watch glass or crystallizing dish, and dry at a temperature not exceeding 50°C. until the leather appears dry; then dry at 105°C. to constant weight as described under the determination of water. Calculate percentage of water-insoluble residue from the dry weight obtained, add to this value the percentages found for water and for fat, subtract the total from 100, and take the difference as percentage of matter soluble in water.

Percentage matter soluble in water = 100 per cent - (percentage water-insoluble residue + percentage water + percentage fat)

Always conduct the determination in duplicate. Agreement of the results within 0.5 per cent is satisfactory. Use one water-insoluble residue for the determination of insoluble ash and the other for the determination of insoluble mineral acid (in vegetable-tanned leather) or insoluble sulfuric acid (in chrome leather).

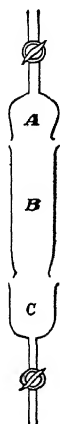


FIG. 7.—Wilson-Kern extractor.

GLUCOSE

Glucose is determined in a portion of the extract obtained in the determination of water-soluble matter by the A. L. C. A. method, or in an extract similarly prepared in case the Wilson-Kern method for water solubles is used. The solution is first freed from matter precipitable by lead, then delead (21), and the higher carbohydrates converted to glucose by boiling with hydrochloric acid. Glucose is then estimated by determining

the quantity of cupric ion that is reduced to cuprous and precipitated when the solution is boiled with Fehling's solution. From the weight of cuprous oxide obtained, the weight of glucose in the solution is obtained from tables empirically worked out by Munson and Walker (Chap. IX). The details of the procedure, embodied in the A. L. C. A. method for glucose (2, 27, 72), must be followed exactly, since even slight variations affect the weight of cuprous oxide obtained. The determination of glucose is required only in the analysis of heavy, vegetable-tanned leathers.

A. L. C. A. Method (2). Copper Sulfate Solution.—Dissolve 69.278 g. of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 1 l. of water and filter through asbestos.

Alkaline Tartrate Solution.—Dissolve 346 g. of Rochelle salt and 100 g. of sodium hydroxide in 1 l. of water. Let the solution stand 2 days and then filter it through asbestos.

Normal Lead Acetate Solution.—Prepare a saturated solution of normal lead acetate.

Dipotassium Phosphate.—Use the phosphate represented by the formula K_2HPO_4 . A solution of this salt in water gives a barely perceptible pink with phenolphthalein. Dry the salt in thin layers at 98 to 100°C. for 16 hr. and keep it in small tightly-stoppered bottles.

Phenolphthalein Solution.—Dissolve 0.25 g. of phenolphthalein in 50 ml. of 95 per cent alcohol.

Determination.—Place 200 ml. of the solution obtained under Water Soluble: Extraction in a 500-ml. flask, add from a pipette 25 ml. of a saturated solution of normal lead acetate, shake frequently for 5 to 10 min., and filter clear, returning the filtrate repeatedly if necessary. Keep funnels covered during this and subsequent filtrations. Collect the clear filtrate in a receiver containing 5.5 g. (not less than 4.5 or more than 6.5 g.) of the dried dipotassium phosphate. Filter off the lead phosphate, letting the funnel drain well. Pipette 150 ml. of the filtrate into an Erlenmeyer flask (500 to 600 ml.) and add from a pipette 7.5 ml. of concentrated hydrochloric acid (sp. gr. 1.18). Also add a pinch (25 mg.) of powdered stearic acid or from 5 to 10 drops of kerosene. Hydrolyze by boiling under a reflux condenser for exactly 2 hr. (Some solutions foam just at the point of boiling. At this stage watch the solution closely, and at the very first sign of foaming turn off the gas. After the foaming subsides, relight immediately. As a rule, no further trouble will be experienced.) After hydrolysis the solution may be allowed to stand at laboratory temperature overnight. Cool to 10 or 15°C., add 2 drops of phenolphthalein solution, carefully neutralize with a solution of sodium hydroxide (1:1) added from a burette and add 0.5 ml. in excess. Without delay transfer to a 200-ml. volumetric flask, dilute to volume, mix, and filter clear. During filtration keep the filtrate just acid by addition from time to time of small portions of pulverized pure tartaric acid. Determine dextrose in the filtrate immediately.

Pipette 50 ml. of the filtrate into a mixture of 25 ml. of the copper sulfate solution and 25 ml. of the alkaline tartrate solution contained in a low form 400-ml. beaker of as near 7 to 8 cm. inside diameter and 9 to 10 cm. depth

as possible. Cover the beaker and heat the solution to 100°C. in exactly 4 min. and continue heating for exactly 2 min., using thermometers to control this operation.¹ Without diluting, filter immediately through asbestos² and wash thoroughly with hot water, then with alcohol, and finally with ether. Dry for $\frac{1}{2}$ hr. at 95 to 100°C., cool, and weigh as cuprous oxide, from which determine the dextrose from Munson and Walker's tables in Chap. IX, and express it as percentage of the leather. Using 15 g. of leather per liter, as prescribed under Water Solubles: Extraction, the 50 ml. aliquot taken for reduction with Fehling's solution is equivalent to 0.5 g. of leather or to one-thirtieth of the charge per liter.

MINERAL ACID IN VEGETABLE-TANNED LEATHER

The determination of mineral acid in vegetable-tanned leather is not a simple matter, and none of the numerous methods that have been proposed is very accurate. The simplest and most widely used method is that originated by Procter and Searle (67), which has received much study and has been adopted in modified form as official by the A. L. C. A. (2). Although subject to numerous errors unless the prescribed conditions of analysis are very carefully followed, the results yielded by this method are sufficiently accurate for the purpose for which it was designed, that is, to show whether or not a leather contains a harmful amount of mineral acid—*provided that the leather is tanned with ordinary vegetable-tanning materials only*. When applied to leathers tanned in part with sulfited or sulfonated materials, however, it may yield results that are wholly misleading (41). It is not possible to extract all the mineral acid from vegetable-tanned leather without decomposing the leather and dissolving some of the acidic organic constituents. This makes it impossible to determine mineral acid by titration. Most of the existing quantitative methods (43, 66, 86) involve the destruction of the organic constituents of the leather. In the Procter-Searle method, the leather is ignited with a known amount of sodium

¹ Adjust the rate of heating before the determination is started. This is best done by adjusting the burner so as to bring 50 ml. of water plus 25 ml. of copper solution plus 25 ml. of tartrate solution contained in a 400-ml. beaker to 100°C. in exactly 4 min.

² Digest finely divided long-fibered asbestos with nitric acid (1:3) for from 2 to 3 days, wash free from acid, and then digest for the same period with 10 per cent sodium hydroxide solution and wash free from alkali. In preparing the Gooch crucible make a bottom layer of about $\frac{1}{4}$ in. with the coarser particles of asbestos and dress off with the fine asbestos. Wash the mat with boiling Fehling's solution, then with nitric acid (1:3), and finally with hot water. Crucibles so prepared can be used for a long time.

carbonate, and the excess alkali determined by titration. In a similar method, originated by Balland and Maljean (67), and modified by numerous workers (43), duplicate samples are ignited with and without carbonate. Sulfate is determined as usual in the ash of both samples, and the excess sulfate present in the ash of the sample ignited with carbonate is calculated as sulfuric acid. In Wuensch's method (67), which Procter thought to be the most accurate known, the leather is oxidized with fuming nitric acid, and total sulfur determined as barium sulfate. The total quantity of bases present that are capable of combining with sulfuric acid is determined, and the sulfate in excess of the amount necessary to combine with these bases is calculated as sulfuric acid. Both the Balland-Maljean method and the Wuensch method assume that the mineral acid present is sulfuric, which is usually, but not always, the case.

One glaring defect which all these methods have in common is that many leathers contain sulfur that is present neither as sulfuric acid nor in combination with a strong base. By the Wuensch method, all this sulfur, including the natural sulfur of the skin, sulfonates, and organic sulfites, is reported as sulfuric acid. By the Procter-Searle method, and probably by the Balland-Maljean method, a large and variable fraction of such sulfur appears as sulfuric acid. This is apt to be very misleading, if, as is frequently the case, the results of the mineral-acid determination are depended upon to tell whether the leather is likely to deteriorate on ageing.

In the absence of sulfites and sulfonates, the Procter-Searle method often gives results that are too low (13, 61, 71, 79, 103), due to reduction of sulfate to sulfite or sulfide during the first stages of incineration and failure to ignite long enough to reoxidize. Too long an ignition is likewise to be avoided, due to danger of volatilizing alkali.

Thomas' phosphate displacement method, which works very well for chrome-tanned leather, has also been applied to vegetable-tanned leather. The principal drawback attending its use is the impossibility of titrating the mineral acid leached from the leather by water in the determination of neutral sulfate. The effect of phosphate on the sulfur-containing radicles of syntans has not been determined.

These defects in the quantitative methods for mineral acid have led to the introduction of many supplementary tests,

qualitative or semiquantitative. The first and simplest of such tests were made with indicators changing at pH values below about 2, applied either to an aqueous extract of the leather or directly to a moistened, freshly cut surface of the leather itself. Bradley and Cohen (16) recommend either thymol blue or xylenol blue. Kohn and Crede (47) determine the pH value of the aqueous extract electrometrically. If the pH value is greater than 3, the leather is considered free from "excess acid"; if it is lower, the excess acid is determined by titrating to pH = 3. Innes (41) recently made a study of the whole subject and concludes that no one test will tell whether a leather contains an excessive amount of mineral acid. He advises three separate determinations: (1) mineral acid by the Procter-Searle method, (2) total sulfate by extraction with sodium carbonate solution (which does not extract sulfonated compounds), and (3) pH value of an aqueous extract of the leather, before and after tenfold dilution. If a strong acid (sulfuric acid, hydrochloric acid, or oxalic acid) is present, the pH value will increase at least 0.7 pH unit after dilution. If a high percentage of acid is indicated by the Procter-Searle method, the results of sodium carbonate extraction will tell whether this is due to sulfuric acid or to sulfonic compounds. Innes' (41) table for interpreting results in all possible cases is given with his procedure.

Atkin and Thompson (4) have just published a new method which seems, in principle, to be the most scientific and accurate yet devised for determining the acidity of leather. This method is based, first, upon the fact that if a jelly is treated with tenth-normal solution of potassium chloride, or other salt, the hydrogen-ion concentration of the external solution becomes practically equal to that of the (melted) jelly. Applied to leather, this means that if leather is treated with tenth-normal potassium chloride solution, the pH value of the solution is the same as the pH value that would be obtained if the leather could be melted and its pH value measured, as can be done in the case of gelatin. But to get enough of the external solution to make a pH determination, a considerable volume of potassium chloride solution must be employed, and hence the acid is diluted. To determine the pH value of the external solution originally present in the leather, Atkin and Thompson make use of the fact that if a number of dilutions are made from a given solution and the pH value of each dilution determined, the plot of the observed pH values

against the logarithms of the dilutions is a straight line. By extrapolating this straight line to zero dilution, the pH value of the undiluted solution can be obtained. Applying this principle to leather, Atkin and Thompson obtain "acidity figures," which they believe to be the pH values of the aqueous acid solution in contact with the fibers of air-dry leather. They find that there is a definite correlation between acidity figures and Procter-Searle mineral-acid percentages, for leathers tanned with ordinary vegetable tanning materials, but that for leathers tanned with syntans, the acidity figures indicate much less free acid than does the Procter-Searle method. These conclusions are fully borne out by experiments conducted in the authors' laboratory.

The Procter-Searle method, as given below, is the official method of the A. L. C. A. (2). In addition, we have given Atkin and Thompson's method for acidity, Innes' method for determining whether a strong acid is present, and Wuensch's method. The latter is very troublesome, and ill-adapted to routine examination of many leathers, but is useful in determining total sulfur in skin or leather of any kind.

The upper limit for permissible mineral acid, as determined by the Procter-Searle method, is not definitely known. Specifications for leather bookbinding (31), in which mineral acid is especially feared because of the long life expected of the bindings, frequently require that the mineral-acid content be less than 0.5 per cent. Other specifications (85) permit up to 1.0 per cent. Certainly a leather containing less than 1 per cent mineral acid (by the Procter-Searle method) can be considered free from objectionable acidity, but it is not necessarily true that leathers containing more than 1 per cent mineral acid by the Procter-Searle method contain a harmful amount of acid.

A. L. C. A. Method for Mineral Acid in Vegetable Leather (Procter-Searle Method).—Place 2 g. of prepared leather in a platinum or rhotanium dish, add 40 ml. of tenth-normal sodium carbonate solution, mix thoroughly, and evaporate to complete dryness on a steam bath. Ignite the residue at a dull red heat, preferably in a muffle furnace, until nearly all of the carbon has been burned off. (If too high a temperature is reached, sodium carbonate will be lost, giving a high value for acidity.) Let the residue cool, moisten it carefully with about 25 ml. of hot water, and break up lumps with a glass rod. Filter into a 300-ml. flask, using an ashless filter paper, and wash four or five times with hot water. Return the filter paper and residue to its dish, dry, and ignite at a dull red heat until all carbon has been burned off. Cool and add to the residue from a burette a quantity of

tenth-normal sulfuric acid exactly equivalent to the sodium carbonate originally added. Cover the dish and heat it on a steam bath for 30 min. If the solution is clear, transfer it quantitatively to the flask containing the first filtrate. If the solution is sufficiently cloudy to interfere with the titration, filter it through a quantitative filter paper into the flask containing the first filtrate, washing the paper with hot water until it is free from acid. Cool the solution and titrate to a clear yellow color with tenth-normal sodium hydroxide or tenth-normal sodium carbonate and 2 or 3 drops of methyl orange solution. Express the result as percentage of sulfuric acid. With each set of determinations run a blank through the entire procedure. If the blank is over 0.3 ml., repeat the determination.

Calculations:

$$\text{Per cent H}_2\text{SO}_4 = \frac{\text{g. sample}}{\text{g. sample}}$$

Wuensch Method (67).—Weigh accurately about 5 g. and drop the leather, piece by piece, into about 50 cc. of cold, fuming nitric acid¹ (sp. g. 1.52). After all the leather has been added and the violence of the reaction has abated, warm gently to complete the oxidation. Let stand overnight. Add about 10 cc. of a 10-per cent solution of barium chloride and enough hydrochloric acid to react with all the nitric acid present. Add the hydrochloric acid in small increments, boiling after each addition, until yellow or brown fumes of chlorine or nitric oxide no longer are given off. Evaporate the solution nearly to dryness, dilute to about 150 cc., add about 5 cc. of hydrochloric acid, and filter the precipitated barium sulfate through Whatman No. 44 filter paper or its equivalent. Wash free from chlorides. Transfer the paper to a weighed crucible, dry at 100°C., and ignite over a good Bunsen burner, allowing free access of air to the interior of the crucible. Cool in a desiccator and weigh as barium sulfate. Calculate percentage of total sulfur as sulfur trioxide.

$$\text{Per cent SO}_3 = \frac{\times 0.343 \times 100}{\text{g. sample}}$$

Then measure the quantity of basic radicals present which are capable of forming non-volatile sulfates with sulfuric acid. To the filtrate from barium sulfate add about 10 cc. of 10-per cent sulfuric acid, let the precipitate settle, and test for complete precipitation of barium by adding a few drops more of sulfuric acid. Let stand overnight. Filter through Whatman No. 44 filter paper or its equivalent, wash free from chlorides, and evaporate the solution nearly to dryness. Transfer the solution to a crucible or small casserole, add about 2 g. of solid ammonium carbonate, evaporate to dryness, and heat till all ammonium salts are expelled. Dissolve the residue in water, filter the solution if necessary, acidify with hydrochloric acid, and precipitate sulfates as barium sulfate, as directed above. Filter, wash, dry, ignite, and weigh as barium sulfate. Calculate percentage of combined sulfur trioxide.

$$\text{Per cent combined SO}_3 = \frac{\text{g. BaSO}_4 \times 0.343 \times 100}{\text{g. sample}}$$

Ordinary nitric acid works about as well.

Take the difference between total and combined sulfate as acid sulfate, and calculate as percentage of sulfuric acid.

Per cent H_2SO_4 = (per cent total SO_3 - per cent combined SO_3) \times 1.225

In this calculation the questionable assumption is made that no sulfuric acid can be present if the basic radicles exceed sulfate radicles in equivalent concentration.

Method of Atkin and Thompson for "Acidity" of Vegetable-tanned Leather.—Weigh three samples of exactly 1, 3, and 9 g., respectively, and treat each with exactly 100 cc. of tenth-normal potassium chloride solution in a Pyrex flask. Stopper and let stand for 24 hr. with occasional shaking. At the same time, weigh a 3-g. sample and determine water by loss in weight as directed in this chapter.

Determine the pH value of the three leather extracts by the hydrogen electrode, or any other method that is accurate to at least 0.1 pH unit (see Chap. VII).

From the weight of water in each sample, calculate the dilution resulting from treatment with 100 cc. of potassium chloride solution. Find the logarithms to base 10 of these dilutions, and plot these logarithms as abscissae and the corresponding pH values as ordinates. The three points thus located should lie practically on a straight line. Project this line till it cuts the axis of pH values. The point of intersection with the axis gives the pH value at zero dilution. Call this pH value the acidity value of the leather.

Example:

FINISHED VEGETABLE-TANNED CALF
 $\text{H}_2\text{O} = 9.6$ Per Cent

Grams sample	Grams H_2O in sample	Dilution	Log_{10} dilution	pH value
1	0.096	0.096	3.02	3.95
3	0.288	$\frac{100.288}{0.288}$	348	3.69
9	0.864	$\frac{100.864}{0.864}$	117	3.57

Acidity value (obtained graphically) = 2.78.

Samples of vegetable-tanned calf leather examined in the authors' laboratory have given acidity values of from 3.0 to 3.5 after tanning; these values are raised as the result of fat liquoring and lowered again practically to the original values as the result of coloring and finishing.

Innes Method (41).—Determine mineral acid by the Procter-Searle method. Determine total sulfate in the leather as follows: Weigh accurately

about 2 g. into a 500-cc. volumetric flask, and digest with 400 cc. of fifth-normal sodium carbonate solution for 24 hr. at room temperature. Make up to volume with water, mix thoroughly, and filter through a dry filter into a dry receiver, discarding the first 20 to 25 cc. of filtrate. Measure 250 cc. of the filtrate into a beaker, acidify with hydrochloric acid, and heat to boiling. Add drop by drop about 10 cc. of a 10-per cent solution of barium chloride. Let stand until the precipitate has settled, preferably overnight. Filter through Whatman No. 44 filter paper or its equivalent, wash until free from chlorides, dry the paper at about 100°C., transfer to a weighed crucible, and ignite over a good Bunsen burner, allowing free access of air. Cool in a desiccator, and weigh. Calculate percentage of total sulfate as sulfur trioxide. Determine pH value of an aqueous extract of the leather and the change in pH value occurring upon tenfold dilution of the extract, as follows: Weigh exactly 1 g. of leather into a small Erlenmeyer flask. Treat with 50 cc. of recently boiled distilled water, stopper, and let stand with occasional shaking for 24 hr. Determine the pH value of the solution by means of the hydrogen electrode, as described in Chap VII. Pipette 10 cc. of the solution into a 100-cc. flask, and make up to the mark with recently boiled distilled water. Determine the pH value of the diluted solution, and call the increase in pH value the "difference figure." Interpret the results of these three tests from the data given in Table 5.

TABLE 5.—INTERPRETATION OF RESULTS OF INNES' TESTS FOR MINERAL ACID IN VEGETABLE-TANNED LEATHER

Difference figure	Procter-Searle mineral acid	Gravimetric sulfate	Conclusions
0.7 to 1.0	Positive	Positive	Sulfuric acid present
0.7 to 1.0	Positive	Negative	Sulfuric acid absent; sulfonic compounds present
0.7 to 1.0	Negative	Positive	Sulfuric acid absent; oxalic acid and neutral sulfates present
0.7 to 1.0	Negative	Negative	Sulfuric acid absent; oxalic acid present
0.6 or less	Positive	Positive	Sulfonic compounds and neutral sulfate present
0.6 or less	Positive	Negative	Sulfonic compounds present; sulfuric acid and sulfates absent
0.6 or less	Negative	Positive	Neutral sulfate present; sulfuric acid and sulfonic compounds absent
0.6 or less	Negative	Negative	Sulfuric acid, sulfates, and sulfonic compounds absent

COMBINED MINERAL ACID

The mineral acid of vegetable-tanned leather is partly removed by washing in the determination of water-soluble matter by the Wilson-Kern method. In order to avoid counting part of the mineral acid twice in calculating fixed tannin, the mineral-acid content of the washed leather must be determined. The result found is used in calculating percentage of fixed tannin but is not reported.

Determine mineral acid in the residue from the determination of water-soluble matter by the Wilson-Kern method, proceeding exactly as directed under A. L. C. A. Method for Mineral Acid. Calculate percentage of combined mineral acid.

SULFURIC ACID AND SULFATE IN CHROME-TANNED LEATHER

Chrome leather practically always contains several per cent of "acid" sulfate, that is, sulfuric acid in combination with a weak base, a combination from which it is readily liberated by hydrolysis, yielding an acid-reacting solution. Most chrome leather contains also a little neutral sulfate. The acid sulfate is combined partly with chromium and partly with the collagen of the leather. To obtain a complete picture of the distribution of sulfate in a chrome leather, it is necessary to determine total sulfate, neutral sulfate, total acid sulfate (by difference), chromium-bound acid sulfate, and protein-bound sulfate (by difference). The separation of acid sulfate into the fractions combined with chromium and with the protein is not generally done as a routine procedure but is valuable in research and in testing special leathers.

Total sulfate is determined by the method originated by Thomas (83), which has been adopted as official by the A. L. C. A. (2). When chrome leather is boiled with a solution of monosodium phosphate, all the sulfate is displaced and can be determined in the solution gravimetrically. Neutral sulfate is determined in a solution obtained by boiling the leather with water. This treatment extracts all the neutral and a small part of the acid sulfate. The extracted sulfate is determined gravimetrically, the small amount of acid sulfate extracted is determined by titration and subtracted from the total, and the remainder taken as neutral sulfate. The difference between total and neutral sulfate is taken as acid sulfate.

Acid sulfate combined with chromium is determined by the "diffusion-neutralization" method, originated by Gustavson (34, 35), and studied in detail by Merrill, Niedercorn, and Quarek (57). A sample of the leather is suspended in water, which is kept at pH = 5.0 — 5.5 by the addition of tenth-normal sodium hydroxide so as to keep the solution just neutral to methyl red. The acid combined with the protein is hydrolyzed, and neutralized by the added alkali as fast as it diffuses from the leather, but the acid combined with the chromium is not appreciably displaced. After 24 hr. the leather is washed, and the acid sulfate remaining in the leather is determined by Thomas' method and taken as chromium-bound acid sulfate. Protein-bound acid sulfate is found by subtracting this value from the total acid sulfate.

A. L. C. A. (Thomas) Method for Total, Neutral, and Combined Acid Sulfate in Chrome Leather (2). *Total Sulfates.*—To 1 g. of leather in a 250-ml. volumetric flask, add 200 ml. of a tenth-normal potassium dihydrogen phosphate, KH_2PO_4 , or sodium dihydrogen phosphate, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, solution. Immerse the flask in a bath of boiling water for 2 hr. Then remove it and cool it to room temperature. Make to volume with distilled water, mix thoroughly, and filter the solution through a folded filter, discarding the first 20 to 25 ml. of the filtrate. Pipette 200 ml. of the filtrate into a 600-ml. beaker, add 5 ml. of hydrochloric acid (1:1), heat to boiling, and while boiling add 20 ml. of a 1-per cent solution of barium chloride, drop by drop. Let the precipitate settle for at least 3 hr., then filter and wash the precipitate well with hot water. Ignite the precipitate, weigh as barium sulfate and calculate to percentage of sulfur trioxide.

Neutral Sulfates.—Using distilled water instead of phosphate solution, proceed exactly as described under Total Sulfates through the first filtration.

a. Pipette 150 ml. of the filtrate into a 400-ml. beaker. Determine sulfates by precipitation with barium chloride and calculate to percentage of sulfur trioxide.

b. Titrate 50 ml. of the filtrate with hundredth-normal sodium hydroxide, using methyl orange as indicator, and calculate to percentage of sulfur trioxide.

The percentage of neutral sulfates equals *a* minus *b*.

Combined Acid Sulfate.—The percentage of combined acid sulfate equals total sulfates minus neutral sulfates.

Calculations:

$$\text{Per cent total SO}_3 = \frac{\text{g. BaSO}_4 \times 0.343 \times 125}{\text{g. sample}}$$

$$[(\text{g. BaSO}_4 \times 0.343 \times 1.667) -$$

$$\{\text{Per cent neutral sulfate, as SO}_3\}] = \frac{-(\text{cc. 0.01-N NaOH} \times 0.0020)}{\text{g. sample}} \times 100$$

Per cent acid sulfate as SO_3 = per cent total SO_3 — per cent neutral SO_3

Per cent acid sulfate as H_2SO_4 = per cent acid sulfate as $\text{SO}_3 \times 1.225$

ANALYSIS OF LEATHER

<p>Diffusion-neutralization Weigh accurately about 2 g. 350 cc. capacity. Treat with Next day add 3 drops fiftieth-normal sodium pink, corresponding to a shaking machine, and color has changed restore the salmon throughout the day salmon-pink end adding alkali if</p>	<p>for ther</p>	<p>Chromium-bound Acid Sulfate (52). a wide-mouth bottle of about water and let stand overnight. pp imatel ges from red to salmon 5.3. Place the bottle in a min. Examine the solution, and if the ough fiftieth-normal sodium hydroxide to Repeat at intervals of from 15 to 30 min. g overnight, titrate the solution to the for 3 hr., examining the solution and hour. Transfer the leather to a Wilson- with running distilled water. Transfer leather to a beaker, and determine sulfate in the leather by the A. L. C. A. method for total sulfate. Calculate and report percentage of acid sulfate combined with chromium (as sulfur trioxide)</p>
--	---------------------	---

$$\text{Per cent Cr-bound SO}_3 = \text{g. } \frac{\text{O}_4 \times 0.343 \times 125}{\text{g. sample}}$$

Protein-bound Acid Sulfate.—Take the difference between total and chromium-bound acid sulfate as protein-bound sulfate.

Per cent protein-bound acid SO₃ = per cent total acid SO₃ —
per cent Cr-bound acid SO₃

COMBINED ACID SULFATE IN CHROME-TANNED LEATHER

This determination is made on the residue from the determination of water-soluble matter, and the results used in calculating fixed organic matter, in order to correct for the sulfuric acid dissolved.

Determine total sulfate by the A. L. C. A. method, employing the residue from the determination of water-soluble matter by the Wilson-Kern method. Calculate as the percentage of insoluble sulfuric acid, and use the result in calculating the percentage of fixed organic matter.

ACIDITY (BASICITY) OF CHROMIUM SALT

The acidity (or basicity) of the chromium complex in the leather is the ratio of equivalents of acid sulfate (or other acid) present to equivalents of chromium present. Thus an acidity of 100 per cent means that all three valences of the chromium present are combined with sulfate, and acidity of 33 per cent means that only one out of the three valences is so combined, etc. Basicity is simply 100 minus per cent acidity; a 100-per cent acid salt is 0-per cent basic, a 33-per cent acid salt is 67-per cent basic, etc.

Strictly speaking, the percentage of sulfur trioxide used in calculating acidity should be the percentage of acid sulfur trioxide combined with chromium, but if this figure is not available the percentage of total acid sulfur trioxide may be used without great error for most leathers.

Calculate percentage of acidity of the chromium complex in the leather as follows:

$$\text{Per cent acidity} = \frac{\text{Per cent SO}_3 \text{ combined with Cr}^* \times 63.35}{\text{Per cent Cr}_2\text{O}_3}$$

* or per cent total acid SO₃

Per cent basicity = 100 — per cent acidity.

A. L. C. A. Method for Basicity (2).—Express basicity according to Schorlemmer's system as described under Chrome Tanning Materials; One Bath Chrome Liquors, Basicity (Chap. X).

HYDROCHLORIC ACID AND NEUTRAL CHLORIDE IN CHROME-TANNED LEATHER

Although most chrome leathers now on the market are tanned with basic chromium sulfate, the tan liquor or the preceding pickle liquor often contains chlorides, so that the leather frequently contains a small percentage of sodium chloride and hydrochloric acid. Some leathers have been tanned exclusively with chromic chloride. In such leathers hydrochloric acid and sodium chloride occupy the same position of importance as do sodium sulfate and sulfuric acid in chromium-sulfate-tanned leathers. Total chloride is determined by ashing the leather in the presence of an excess of sodium carbonate. Neutral chloride is determined in the ash obtained in the absence of sodium carbonate. Hydrochloric acid is determined by difference.

Total Chloride.—Weigh accurately about 3 g. into a platinum dish, moisten thoroughly with 10-per cent sodium carbonate solution (about 15 cc.), evaporate to dryness on the water bath, and ignite, preferably in an electric muffle furnace, at dull red heat until the leather is completely carbonized. Extract the charred mass four times with 10 to 15 cc. of hot water, filter, save the filtrate, return the paper to the dish, and complete the ashing at bright red heat. Treat the ash with 25 cc. of 10-per cent acetic acid, heat to boiling, and rinse into the beaker containing the filtrate previously obtained. Add a drop of phenolphthalein, and add more 10-per cent acetic acid, if necessary, to make the solution acid. A slight excess of acetic acid does no harm. Add a few drops of potassium chromate indicator,

and titrate with tenth-normal silver nitrate until a permanent brick-red precipitate is produced.¹ Calculate percentage of total chloride.

$$\text{Per cent Cl} = \frac{\text{cc. } 0.1\text{-}N \text{ AgNO}_3 \times 0.003546 \times 100}{\text{g. sample}}$$

Neutral Chloride.—Proceed exactly as described above, omitting the sodium carbonate. Calculate percentage of neutral chloride as chlorine, or as sodium chloride if desired.

$$\text{Per cent neutral Cl} = \frac{\text{cc. } 0.1\text{-}N \text{ AgNO}_3 \times 0.003546 \times 100}{\text{g. sample}}$$

$$\text{Per cent NaCl} = \frac{\text{cc. } 0.1\text{-}N \text{ AgNO}_3 \times 0.005846 \times 100}{\text{g. sample}}$$

Acid Chloride.—Take the difference between total and neutral chloride as acid chloride. Calculate and report as percentage of hydrochloric acid.

$$\text{Per cent HCl} = (\text{total Cl} - \text{per cent neutral Cl}) \times 1.028$$

A method similar to that employed for determining acid and neutral sulfate has been proposed by Thomas and Frieden (84) for acid and neutral chloride. Total chloride is determined by extraction with tenth-molar disodium phosphate, exactly as described in the A. L. C. A. method for sulfate. Neutral chloride is determined by extraction of the leather with 95-per cent alcohol. This extraction removes about 25 per cent of the chloride from leathers presumably containing no neutral chloride, and hence the determination of acid chloride is in error to that extent.

COMBINED TANNIN (OR OTHER ORGANIC MATTER)

The difference between 100 per cent and the sum of the percentages of all the other constituents is taken as percentage of combined organic matter. In the case of vegetable-tanned or chrome-tanned leather retanned with vegetable-tanning material, this consists of fixed tannin, plus coloring and other insoluble organic matter. In the case of oil-tanned, aldehyde-tanned, or syntan-tanned leathers, the fixed organic matter obviously consists of fixed oil, fixed aldehyde, or fixed syntan. The calculation of fixed organic matter offers no difficulty except that care must be taken not to count any constituent twice. For this reason the percentages of *insoluble* ash and a *combined* mineral acid (or *combined* acid sulfate in chrome leather) are used instead

¹ If desired, the determination may be made by the Volhard method (Chap. VIII).

of total ash and total acid, which contribute in part to the percentage of water-soluble matter found.

Authors' Method for Combined Organic Matter (Tannin).—Add the percentages found for (1) water, (2) fat (chloroform extract), (3) hide substance, (4) water-soluble matter (Wilson-Kern method), (5) insoluble ash, and (6) combined mineral acid (in vegetable-tanned leather) or combined acid sulfate as sulfuric acid (in chrome-tanned leather). Subtract the total from 100 per cent and report the difference as percentage of fixed organic matter (tannin).

A. L. C. A. Method for Combined Tannin in Vegetable-tanned Leather(2). The difference between 100 and the sum of the percentages of moisture, insoluble ash, petroleum ether extract, hide substance, and soluble solids is the percentage of combined tannin.

COMPOSITIONS OF TYPICAL LEATHERS

Except in the comparatively rare cases in which leather is bought on specifications that include a definite chemical composition as part of the requirements, the analysis of leather is of much greater interest to the tanner than to the purchaser. The latter is vitally interested in the physical properties of the leather, including those discussed in Chap. IV, as well as others which are almost impossible to define or measure but is interested in the composition of the leather only as it influences these properties. The tanner is, of course, just as vitally interested in producing a leather possessing the properties desired by his customers, but, unlike those customers, he is in a position to determine the effect upon those properties of variations in the chemical composition of his product. Each tanner must determine for himself the effect of variations in composition upon the quality of each kind of leather produced in his establishment. It is not, and probably never will be, possible to state that the ideal sole leather, for example, should contain so many per cent of hide substance, so many per cent of fat, so many per cent of fixed tannin, and so on. The analyses tabulated below are merely those of typical leathers of various kinds.

Wilson and Lines (99) have published the analyses of 18 different kinds of shoe leather, described more fully in Chap. IV. They used the A. L. C. A. methods with the following exceptions. Fat was determined by extraction with chloroform. After extraction with chloroform, the patent leathers were extracted further with a mixture of ethyl acetate and acetone for several days and the residue from this further extract was called collodion. The nitrogen content of these residues was determined and found

TABLE 6.—ANALYSES OF 18 TYPICAL SHOE LEATHERS (95)
Percentage

Type of leather	Water pro- tein N X 5.62	Fat	H ₂ SO ₄	Na ₂ SO ₄	HCl	NaCl	CaO	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	CaSO ₄	MgSO ₄	Collo- dion	Or- ganic water solu- ble	Com- bined tannin (by differ- ence)	Other or- ganic matter (by differ- ence)	Total
Colored, vegetable- tanned calf.....	13.6	41.0	12.0	0.3	0.4	0.1	9.1	23.5	100.0
Colored, chrome- tanned calf.....	16.3	62.6	4.6	3.4	0.4	0.3	0.5	1.2	0.3	5.4	5.0	100.0
Black, chrome-tanned, glazed kid.....	13.7	65.3	6.6	1.0	0.9	0.5	0.2	0.2	0.3	4.5	6.6	100.0
Black, chrome-tanned kangaroo.....	12.0	62.7	11.3	1.3	0.2	0.3	0.1	0.3	0.1	6.0	5.1	100.0
Black, vegetable- tanned horse butt (cordovan).....	10.0	40.1	18.6	0.6	0.1	...	0.1	8.7	21.8	100.0
Colored, chrome-tan- ned buffed and split cowhide (buck).....	14.1	69.6	2.1	3.2	0.3	0.2	1.0	0.6	5.3	3.6	100.0
Colored, chrome-tanned side (split cowhide)...	16.3	66.8	5.8	3.6	1.0	0.3	0.1	0.2	3.6	2.1	100.0
Black, chrome-tanned slink calf (suede)...	12.7	55.1	7.1	0.8	0.4	0.2	0.1	0.2	1.0	1.2	5.4	15.8	100.0
Uncolored, vegetable- tanned calf (shoe lining).....	11.9	46.0	7.6	0.1	0.2	0.1	12.3	21.8	100.0
Uncolored, vegetable- tanned sheep (shoe lining).....	10.9	50.0	6.1	1.7	0.6	0.1	0.1	0.1	13.0	17.4	100.0

Black, vegetable-tanned shark.....	12.2	45.4	6.9	1.5	5.4	28.4	100.0
Patent, chrome-tanned side (split cowhide)...	10.1	50.5	10.0	1.8	0.6	0.1	...	0.1	0.4	2.9	14.4	100.0
Patent, chrome-tanned kid.....	11.8	54.0	6.6	2.1	0.3	0.2	0.6	3.6	12.2	100.0
Patent, chrome-tanned colt.....	12.0	60.4	5.1	2.3	0.5	0.1	0.1	0.3	0.1	3.6	9.1	100.0
Heavy, black, chrome-tanned cowhide.....	14.4	57.0	14.2	4.4	0.4	0.1	0.4	5.5	2.9	100.0
Chrome-tan, army upper leather.....	15.1	44.6	20.4	1.1	0.3	...	0.4	...	0.3	0.2	2.4	...	15.2	100.0
Vegetable-tanned steer hide (sole leather)...	14.6	29.7	3.2	0.8	100.0
Chrome-tanned steer hide (sole leather)...	16.3	29.4	25.4	5.9	12.3	0.8	0.9	...	2.6	0.5	1.7	2.3	0.5	100.0

to be as follows: patent side, 11.8 per cent; patent kid, 10.5 per cent; and patent colt, 12.6 per cent. Water-soluble matter was determined by the Wilson-Kern method. In the chrome leather analyses, sulfuric acid represents what is called combined acid sulfate in the A. L. C. A. method. The difference between total water soluble matter and soluble ash was called organic water soluble matter and is so reported. A correction was made, where necessary, for the mineral acid washed out in the determination of water soluble. "Other organic matter" in the chrome leathers consists of fixed organic matter plus the almost negligibly small percentage of organic water soluble. Instead of reporting ash determinations, it was considered sufficient to report the inorganic constituents separately, making the sum of the percentages equal 100. It is quite apparent which is soluble.

The two samples of sole leather were furnished as bends and were prepared for analysis by shaving. All other leathers were sampled and cut up by the authors' method, described in this chapter. All samples were brought to equilibrium with an atmosphere of 50-per cent relative humidity before analysis, and

TABLE 7.—ANALYSES OF OAK BELTING

Constituent	Balderston	Bowker
Water.....	10.5	8.86
Hide substance.....	40.4	41.73
Grease (petrolie ether extract).....	11.05	11.37
Water-soluble (A. L. C. A. method)...	13.3	13.96
Insoluble ash.....	0.23
Combined tannin (by difference).....	24.51	23.85
Soluble tannin.....	9.1	10.28
Soluble non-tannin.....	4.2	3.68
Glucose.....	Trace
Epsom salt.....	Trace
Acid (as sulfuric).....	0.20
Total ash.....	0.24	0.25
Percentage unsaponifiable in grease...	24.8
pH value (100 cc. extract from 4.9 g. dry leather).....	3.24

Furnished by Lloyd Balderston of J. E. Rhodes & Sons, Wilmington, Del. Two pieces, about 3.25 by 48 in., were cut from the same hide about 4 to 7 in. from the backbone, one from either side symmetrically placed. Before any tests were made, the leather was kept for 48 hr. in an atmosphere of 50-per cent relative humidity. Analyses were made on strips cut the entire length of the samples.

TABLE 8.—ANALYSES OF VEGETABLE-TANNED SIDE LEATHERS

Constituent	"2.5-oz. grain"		"Deep buff"	
	Blair	Bowker	Blair	Bowker
Water.....	9.3	6.62	10.9	8.13
Dry basis				
Hide substance.....	44.8	44.06	54.9	54.55
Grease (petrolie ether extract).....	12.4	14.41	7.3	8.01
Water soluble (A. L. C. A. method).....	7.3	7.94	9.9	10.07
Insoluble ash.....	0.14	0.08
Combined tannin (by difference).....	35.5	33.45	27.9	27.29
Soluble tannin.....	5.23	8.33
Soluble non-tannin.....	2.71	1.74
Glucose.....	None	Trace
Epsom salt.....	0.24	0.24
Acid (as sulfuric).....	0.9	0.84	0.3	0.28
Total ash.....	0.7	0.70	0.3	0.34

Furnished by Norman Hertz of Max Hertz Leather Co., Newark, N. J. The leather was made from domestic packer hides, tanned entirely with vegetable tanning materials and fat liquored with a mixture of neutral and sulfonated oils. The analysis was made for Mr. Hertz by C. A. Blair.

TABLE 9.—ANALYSES OF VEGETABLE-TANNED SOLE LEATHER

Constituent	Bends		Backs	
	Porter	Bowker	Porter	Bowker
Water.....	9.82	7.99	8.60	8.87
Dry basis				
Hide substance.....	34.40	33.98	33.26	34.50
Grease (petrolie ether extract).....	5.12	4.89	5.22	5.92
Water soluble (A. L. C. A. method).....	36.89	34.70	36.97	35.34
Insoluble ash.....	0.14	0.13	0.14	0.16
Combined tannin (by difference)....	23.45	26.30	24.41	24.08
Soluble tannin.....	17.57	16.14	18.05	16.54
Soluble non-tannin.....	19.32	18.56	18.92	18.79
Glucose.....	8.63	8.92	8.93	8.23
Epsom salt.....	5.33	5.18	5.57	5.97
Acid (as sulfuric).....	0.74	0.55	0.58	1.12
Total ash.....	4.55	4.76	4.35	4.59
Iron (as ferric oxide).....	0.01	0.02	

Furnished by R. E. Porter of Ashland Leather Co., Ashland, Ky. The bends, called "heavy finders' sole leather," were made from native packer steer hides. The backs, called "manufacturers' backs," were made from native packer cowhides.

the water contents are significant as representing the amount held by the leather under such conditions.

In connection with an investigation of the properties of leather, a committee of the A. L. C. A. has recently furnished analyses of a number of other typical leathers. These analyses are given below (95). In each case two sets of analyses are given, one by the chemist furnishing the leather and the other by R. C. Bowker, of the Bureau of Standards.

TABLE 10.—ANALYSES OF MISCELLANEOUS CHROME LEATHERS

Constituent	Retan sole	Horse garment	Horse glove	Calf upper	Side upper
Water (O)*.....	11.71	5.08	4.67	15.06	14.14
(B).....	8.36	6.60	9.04	9.26	10.28
Hide substance (O).....	65.95	52.34	58.49	74.38	74.82
(B).....	63.90	44.21	58.88	74.18	72.14
Grease (petrol extract) (O)....	11.26	26.19	8.26	1.75	1.65
(B).....	13.25	29.61	9.11	1.53	2.43
Ash (O).....	3.24	3.66	9.65	5.94	6.01
(B).....	3.30	3.95	9.38	6.06	7.05
Chromic oxide (O).....	2.70	3.34	7.42	5.60	4.98
(B).....	2.52	3.13	6.37	5.39	5.50
Ferric oxide plus aluminum oxide (O).....	0.28	0.14	1.77	0.28	0.52
(B).....	0.25	0.10	0.84	0.23	0.51
Total sulfate (as sulfur trioxide) (O).....	1.34	0.71	1.30	2.80	1.46
(B).....	1.28	1.04	1.42	3.40	2.41
Neutral sulfate (as sulfur tri- oxide) (O).....	0.25	0.19	0.28	0.20	0.17
(B).....	0.24	0.23	0.47	0.24	0.36
Acid sulfate (as sulfuric acid) (O).....	1.34	0.64	1.25	3.19	1.58
(B).....	1.27	0.99	1.16	3.87	2.51
Total chlorine (O).....	0.08	0.04	0.08	0.04	0.03
(B).....	0.18	0.12	0.08	0.08	0.08

* (O) indicates results by Orthmann; (B), results by Bowker.

Furnished by A. C. Orthmann of Pfister and Vogel Leather Co., Milwaukee, Wis. The "retan-sole" leather was tanned by a one-bath chrome and then retanned in chestnut liquor until just struck through. It was then dried and treated to render it water resisting. The "horse-garment" leather was chrome tanned, blacked in the drum, and finished by hand, with full grain, to make it water resistant. The "horse-glove" leather was tanned by the two-bath chrome process, fat liquored with sod oil and

tallow soap, buffed, colored in the drum, and finished by hand. The "calf upper" is calf tanned by the one-bath process, colored in the drum, and finished by hand. The "side-upper" leather was tanned and finished like the calf, except for a slight snuffing of the grain before finishing. Mr. Orthmann was assisted in his work by William Arner.

EFFECT OF LOCATION (95)

Leather is not of uniform chemical composition throughout its volume; on the contrary, its composition varies greatly from the grain surface to the flesh surface, from head to tail, and from belly to backbone. The variations follow general rules, however, so that one can study these variations intelligently and use them. A definite variation in composition from grain to flesh is usually necessary to give the leather certain desired properties.

In order to study the variation in composition from grain to flesh, it is necessary to split the sample into a number of thin layers, each of which is analyzed separately. This can be done either on a big tannery splitting machine or on a skiving machine, such as is used in shoe factories. The skiving machine is usually so small as to make a useful laboratory splitting machine for very small samples. A type found suitable for laboratory work by the authors is the Pluma, model E.¹

Analyses of splits made on this machine of finished calf leather were made in the authors' laboratories by H. B. Merrill. Table 11 shows the variation in composition of vegetable-tanned calf leather from grain to flesh and Table 12 gives similar values for

11.—ANALYSES OF COLORED, VEGETABLE-TANNED CALF LEATHER AT DIFFERENT DEPTHS FROM GRAIN SURFACE

Position of split	Grain	Second layer	Third layer	Fourth layer	Flesh
Average thickness, millimeters...	0.24	0.28	0.46	0.32	0.24
Water.....	9.6	10.9	12.3	12.3	10.6
Skin protein (nitrogen $\times 5.62$)...	35.9	42.8	48.2	46.2	42.1
Fat (chloroform extract).....	19.4	14.3	7.0	9.9	13.4
Sulfuric acid.....	0.7	0.7	0.3	0.4	0.3
Aluminum oxide plus ferric oxide.	2.5	0.9	0.4	0.6	1.2
Organic water soluble.....	7.7	12.3	13.8	14.1	10.0
Combined tannin (by difference).	24.2	18.2	18.0	16.5	22.4
	100.0	100.0	100.0	100.0	100.0

¹ Made by United Shoe Machinery Corporation, Boston, Mass.

chrome-tanned calf leather. The fat content is greater in the surface layers because steps are taken to prevent complete diffusion throughout the thickness, which would make the leather too soft and raggy. The higher tannin content at the surfaces is due to the longer period of contact with tan liquor, which diffuses very slowly into skin. The lower chromium content at the surfaces is due to a stripping of the chromium from the surfaces in certain operation following tanning. The

TABLE 12.—ANALYSES OF COLORED, CHROME CALF LEATHER AT DIFFERENT DEPTHS FROM GRAIN SURFACE

Position of split	Grain	Second layer	Third layer	Fourth layer	Flesh
Average thickness, millimeters...	0.13	0.20	0.33	0.22	0.22
Water.....	10.4	12.3	14.2	14.6	11.6
Skin protein (nitrogen \times 5.62)...	53.0	64.9	72.5	70.8	60.6
Fat (chloroform extract).....	16.1	4.7	0.7	2.4	11.1
Sulfuric acid.....	2.0	3.9	4.8	4.3	2.2
Sodium sulfate.....	0.2	0.3	0.2	0.2	0.1
Chromic oxide.....	6.0	6.9	6.4	6.1	5.4
Aluminum plus ferric oxide.....	3.6	1.8	0.4	0.5	1.5
Sodium chloride plus hydrochloric acid.....	0.0	0.4	0.8	0.5	0.0
Other organic matter (by difference).....	8.7	4.8	0.0	0.6	7.5
	100.0	100.0	100.0	100.0	100.0

TABLE 13.—ANALYSES OF RUSSET, VEGETABLE-TANNED SIDE LEATHER AT DIFFERENT DEPTHS FROM GRAIN SURFACE

Position of split	Grain	Second layer	Third layer	Fourth layer	Flesh
Average thickness, millimeters...	0.85	0.75	0.60	0.80	0.50
Water.....	13.6	13.9	13.7	14.1	13.6
Skin protein (nitrogen \times 5.62)...	39.3	42.9	45.4	47.8	45.0
Fat (chloroform extract).....	11.0	7.0	4.3	2.6	5.6
Sulfuric acid.....	0.8	0.9	1.1	1.1	1.1
Aluminum oxide plus ferric oxide.....	0.2	0.0	0.0	0.0	0.0
Organic water soluble.....	7.9	6.9	7.8	6.5	6.9
Combined tannin (by difference).....	27.2	28.4	27.7	27.9	27.8
	100.0	100.0	100.0	100.0	100.0

area covered by the analyses of these two calfskins was a rectangle 20 in. long and 16 in. wide centered on the skin.

Similar analyses of strap, harness, and skirting leathers are given in Tables 13 to 15. The analyses were made in the authors' laboratories by E. J. Kern and R. M. Olson.

TABLE 14.—ANALYSES OF BLACK, VEGETABLE-TANNED HARNESS LEATHER AT DIFFERENT DEPTHS FROM GRAIN SURFACE

Position of split	Grain	Second layer	Third layer	Fourth layer	Flesh
Average thickness, millimeters...	1.80	0.75	0.56	0.75	1.12
Water.....	9.0	12.5	12.2	12.3	9.0
Skin protein (nitrogen \times 5.62)...	25.2	39.8	40.3	37.2	27.9
Fat (chloroform extract).....	38.3	16.9	16.5	20.6	33.9
Sulfuric acid.....	0.2	0.2	0.3	0.2	0.4
Barium sulfate (loading material)	5.3	0.0	0.0	0.0	4.5
Organic water soluble.....	6.2	8.8	9.4	8.4	7.0
Combined tannin (by difference)...	15.8	21.8	21.3	21.3	17.3
	100.0	100.0	100.0	100.0	100.0

TABLE 15.—ANALYSES OF VEGETABLE-TANNED, OIL-SKIRTING LEATHER AT DIFFERENT DEPTHS FROM GRAIN SURFACE

Position of split	Grain	Second layer	Third layer	Fourth layer	Flesh
Average thickness, millimeters...	1.00	1.50	0.50	0.50	1.00
Water.....	11.8	12.8	13.1	13.0	11.6
Skin protein (nitrogen \times 5.62)...	39.8	45.0	46.2	45.3	41.4
Fat (chloroform extract).....	8.4	3.9	3.6	5.1	10.1
Sulfuric acid.....	0.6	0.8	0.7	0.7	0.6
Aluminum oxide plus ferric oxide.	0.1	0.1	0.1	0.1	0.4
Organic water soluble.....	15.5	15.8	16.8	15.2	14.2
Combined tannin (by difference)...	23.8	21.6	19.5	20.6	21.7
	100.0	100.0	100.0	100.0	100.0

The variation in composition over the area of leather follows certain general rules. In fat liquoring, the skin tends to take up the same amount of fat per unit area all over the skin. The shoulder portion is usually thinner than the butt and thus gets more fat per unit weight because it gets the same amount per unit area. This rule holds very well for portions of the leather of

equally tight structure but is modified by variations in the structure, such as exist between the butt and belly regions, which are usually of equal thickness. The looser structure of the belly region causes a greater rate of absorption of fat, and thus the belly region gets more per unit area than the butt as well as more per unit weight. Similar rules hold for the absorption of tannins and other materials.

Fleming and Lathrop, working in the authors' laboratories, have analyzed the butt and belly portions of both chrome- and vegetable-tanned calf leathers. Each butt sample was a strip 4 by 20 in. with length running parallel to the line of the backbone and about 4 in. from it and with the lower end about 4 in. from the tail end of the skin. The belly samples were strips 3.5 in.

16.—COMPARISON OF CHEMICAL COMPOSITIONS OF BUTT AND BELLY PORTIONS OF COLORED, VEGETABLE-TANNED CALF LEATHER

Constituent	Butt	Belly
Water.....	11.6	10.9
Skin protein (nitrogen \times 5.62)...	41.8	38.4
Fat (chloroform extract).....	10.8	15.1
Sulfuric acid.....	0.8	0.6
Aluminum oxide plus ferric oxide	0.6	0.8
Organic water soluble.....	7.1	5.7
Combined tannin (by difference).	27.3	28.5
	100.0	100.0

TABLE 17.—COMPARISON OF CHEMICAL COMPOSITIONS OF BUTT AND BELLY PORTIONS OF COLORED, CHROME-TANNED CALF LEATHER

Constituent	Butt	Belly
Water.....	13.0	14.8
Skin protein (nitrogen \times 5.62).....	71.4	66.9
Fat (chloroform extract).....	5.2	6.5
Sulfuric acid.....	3.3	1.8
Sodium chloride.....	0.5	0.4
Aluminum oxide.....	0.4	0.4
Ferric oxide.....	0.1	0.2
Chromic oxide.....	3.1	3.2
Other organic matter (by difference).....	3.0	5.8
	100.0	100.0

wide, following the contour of the skin at the extreme right side of the skin, with ends just opposite those of the butt samples. The analyses are given in Tables 16 and 17.

References

1. ALSOP, W. K.: Determination of Oil and Grease in Leather. Committee Report, *J. Am. Leather Chem. Assoc.*, **17**, 292-305, 1922.
2. AMERICAN LEATHER CHEMISTS ASSOCIATION: Methods of Analysis, *J. Am. Leather Chem. Assoc.*, **22**, 567-593, 1927.
3. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS: "Methods of Analysis," 2d ed., 1925; Changes in Methods of Analysis, *J. Assoc. Official Agric. Chem.*, **10**, 31, 1927.
4. ATKIN, W. R., and F. C. THOMPSON: Acidity of Vegetable-tanned Leather, *J. Intern. Soc. Leather Trades Chem.*, **13**, 300-309, 1929.
5. BALDERSTON, L.: Analysis of Chrome Leather Containing Barium, *J. Am. Leather Chem. Assoc.*, **18**, 491-492, 1923.
6. BALDERSTON, L., et al.: Determination of Chromium in Chrome Leather, Committee Report, *ibid.*, **18**, 441-444, 1923.
7. BALDERSTON, L.: Extraction of Grease from Leather, *ibid.*, **18**, 475-480, 1923.
8. BALDERSTON, L.: Preparation of Leather for Analysis, *ibid.*, **18**, 154-160, 1923; **20**, 583-590, 1925.
9. BALDERSTON, L., et al.: Determination of Nitrogen in Leather, Committee Report, *ibid.*, **22**, 261, 1927.
10. BALDERSTON, L., and W. K. ALSOP: Extractor for Water-soluble Matter in Leather, *ibid.*, **13**, 142-144, 1918.
11. BENNETT, H. G.: Analysis of Limed Pelt, *Collegium*, London ed., 85-89, 1916; *J. Am. Leather Chem. Assoc.*, **12**, 12-18, 1917.
12. BIDWELL, G. L., and W. F. STERLING: Preliminary Notes on Direct Determination of Moisture, *Ind. Eng. Chem.*, **17**, 147, 1925.
13. BLACKADDER, T.: Determination of Free H_2SO_4 in Vegetable-tanned Leather, Committee Report, *J. Am. Leather Chem. Assoc.*, **20**, 277-282, 1925.
14. BLOCKEY, J. R.: Vegetable Sole Leather Analysis, *J. Soc. Leather Trades Chem.*, **9**, 307, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 486, 1925.
15. BOWKER, R. C., and E. L. WALLACE: Sampling of Leather for Chemical Analysis, *J. Am. Leather Chem. Assoc.*, **17**, 217-220, 1922.
16. BRADLEY, H., and A. COHEN: Indicator Test Paper for Acidity in Leather, *J. Soc. Leather Trades Chem.*, **8**, 340, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 190, 1925.
17. CHAMBERD, P., et al.: Analysis of Vegetable-tanned Leather, Committee Report, *J. Intern. Soc. Leather Trades Chem.*, **13**, 355-365, 1929.
18. CHAMBERD, P., et al.: Hide Analysis, Committee Report, *ibid.*, **5**, 313-322, 1921; abstracted in *J. Am. Leather Chem.*, **17**, 133, 1922.
19. CHURCHILL, J. B., et al.: Determination of Free Sulfuric Acid in Leather, Committee Report, *J. Am. Leather Chem. Assoc.*, **14**, 330-348, 1919.
20. CLARKE, I. D., and R. W. FREY: Comparison of Four Machines in the Preparation of Leather Samples for Analysis, *ibid.*, **23**, 412-426, 1928.

21. CLARKE, I. D., and R. W. FREY: Effect of Certain Deleading Agents upon Hydrolysis in the Determination of Reducing Solutions in Leather and Tanning Extracts, *ibid.*, **19**, 237-249, 1924.

22. COLIN-RUSS, A.: Estimation of Fat and Water Solubles in Leather: I, *J. Intern. Soc. Leather Trades Chem.*, **9**, 455, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 223, 1926.

23. DEAN, E. W., and D. D. STARK: Determination of Water in Petroleum and Other Organic Emulsions, *Ind. Eng. Chem.*, **12**, 486, 1920.

24. DRESSING LEATHER COMMITTEE OF THE I. S. L. T. C.: Extraction of Grease from Leather, *J. Soc. Leather Trades Chem.*, **4**, 300, 1920; abstracted in *J. Am. Leather Chem. Assoc.*, **16**, 221, 1921.

25. ENNA, F. G. A.: Determination of Fat in Leather, *J. Intern. Soc. Leather Trades Chem.*, **13**, 37, 1929; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 428, 1929.

26. FREY, R. W., *et al.*: Comparison of Boric Acid and Hydrochloric Acid in the Determination of Nitrogen in Leather, *J. Am. Leather Chem. Assoc.*, **21**, 583-587, 1926.

27. FREY, R. W., *et al.*: Determination of Sugar Content of Leather, Committee Report, *ibid.*, **19**, 339-354, 1924.

28. FREY, R. W.: Device for Preparing Light Leather Samples for Analysis, *ibid.*, **20**, 470-475, 1925.

29. FREY, R. W., and I. D. CLARKE: Determination of Water-soluble Matter in Leather, *ibid.*, **14**, 488-499, 1919.

30. FREY, R. W., L. J. JENKINS, and H. M. JOSLIN: Comparison of Several Methods of Hydrolysis in Determining Nitrogen in Leather, *ibid.*, **23**, 397-402, 1928.

31. FREY, R. W., L. R. LEINBACH and E. O. REED: Analysis of Some English Book-binding Leathers, *ibid.*, **24**, 190-196, 1929.

32. GERNGROSS, O., and W. E. SCHAEFER: Micro-Kjeldahl Method for Technical Tanning and Similar Investigations in Industries Working with Proteins, *Collegium*, 187, 1923.

33. GOLDENBURG, A. M.: Chemicooanalytical Standards in Leather Manufacture, *Collegium*, **10**, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 298, 1927.

34. GUSTAVSON, K. H.: Acidity of Chrome Leather, *J. Am. Leather Chem. Assoc.*, **22**, 60-69, 1927.

35. GUSTAVSON, K. H.: The Sulfato-hydroxo-chromi-collagen Compound, *ibid.*, **21**, 559-570, 1926.

36. HARVEY, A.: "Practical Leather Chemistry," 152-177, Crosby Lockwood and Son, London, 1920.

37. HEY, A. M.: Influence of Moisture on the Extraction of Oils and Grease from Leather, *J. Soc. Leather Trades Chem.*, **6**, 385, 1922.

38. HOU, TE-PANG: Volumetric Determination of Chromium in Chrome Leather, *J. Am. Leather Chem. Assoc.*, **15**, 367-374, 1920.

39. HUDSON, F.: Analysis of Chrome Leathers, *J. Intern. Soc. Leather Trades Chem.*, **11**, 133, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 653, 1927.

40. INNES, R. F., *et al.*: Analysis of Chrome Leathers and Liquors, Committee Report, *J. Soc. Leather Trades Chem.*, **7**, 413, 1923; **9**, 508, 1925.

41. INNES, R. F.: Determination of Acid in Leather, *ibid.*, **12**, 256-272, 1928.
42. JABLONSKI, L., *et al.*: Leather Analysis, Committee Report, *Collegium*, 177, 1927.
43. JALADE, E.: Sulfuric Acid Acidity of Leather, *Halle aux Cuirs*, 129, 1924; *Cuir*, **13**, 120, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 546, 1924.
44. JARAMILLO, G.: Rapid Method for Determination of Organic Nitrogen, *J. Am. Chem. Soc.*, **48**, 2,453, 1926.
45. JARRELL, T. D. (referee): Report on Tanning Materials and Leather, *J. Assoc. Official Agric. Chem.*, **10**, 143-150, 1927.
46. KELLY, M. W.: Nitrogen Content of Hide Powder, *J. Am. Leather Chem. Assoc.*, **21**, 573-580, 1926.
47. KOHN, S., and E. CREDE: Acidity of Vegetable-tanned Leather, *ibid.*, **18**, 189-194, 1923.
48. LATSHAW, W. L.: Sodium Sulfate as a Substitute for Potassium Sulfate in the Gunning Modification for Determining Nitrogen, *ibid.*, **11**, 454, 1916.
49. LAUFFMANN, R.: Investigation of Leather and its Valuation upon the Analytical Results, *Gerber*, **50**, 25, 33, 41, 49, 1924.
50. LAUFFMANN, R.: Solvent Action and Use of Different Solvents for the Determination of Fat in Leather, *Ledertech. Rundschau*, **19**, 63, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 143, 1929.
51. LEVI, L. E., *et al.*: Analysis of Chrome Leather, Committee Report, *J. Am. Leather Chem. Assoc.*, **15**, 269-273, 1920.
52. LEVI, L. E., and A. C. ORTHMANN: "Laboratory Manual," 16-20, 77-85, Pfister & Vogel Leather Co., Milwaukee, Wis., 1918.
53. LEVI, L. E. and A. C. ORTHMANN: Determination of Fat in Leather, *J. Am. Leather Chem. Assoc.*, **13**, 313-318, 1918.
54. LITTLE, E., and E. SARGENT: Analysis of Chrome-tanned Leather, *ibid.*, **18**, 659-662, 1923.
55. MERRILL, H. B.: Action of Water on Vegetable-tanned Leather: I, Rate of Removal of Uncombined Soluble Matter, *ibid.*, **24**, 235-242, 1929; II, Resistance of the Collagen-tannin Compound to Hydrolysis upon Long Washing, *ibid.*, **25**, 173-182, 1930.
56. MERRILL, H. B.: Modified Wilson-Kern Extractor, *ibid.*, **24**, 244-245, 1929.
57. MERRILL, H. B., J. G. NIEDERCORN, and R. QUARCK: Determination of Sulfato-groups in Chrome Leather, *ibid.*, **23**, 187-208, 1928.
58. MOSSER, T. J., *et al.*: Determination of Soluble Matter in Leather, Committee Report, *ibid.*, **20**, 378-382, 1925.
59. MUDD, J. S., and P. L. PEBODY: Acidity Control of Chrome Leather, *J. Intern. Soc. Leather Trades Chem.*, **13**, 205-214, 1929.
60. OBERFELL, C. R.: Extractor for Water-soluble Material for Leather, *J. Am. Leather Chem. Assoc.*, **11**, 219-221, 1916.
61. OBERFELL, C. R.: Free Sulfuric Acid in Leather, *ibid.*, **12**, 344-347, 1917.
62. ORTHMANN, A. C., *et al.*: Chrome Leather, Committee Report, *ibid.*, **19**, 191-196, 1924; **20**, 201-204, 1925.

63. ORTHMANN, A. C.: Machine for Preparing Leather Samples for Analysis, *ibid.*, **20**, 579-583, 1925.

64. ORTHMANN, A. C.: Method for Evaluating Raw Stock, *ibid.*, **23**, 1-3, 1928.

65. PAGE, R. O.: Determination and Nature of Water Solubles in Leather Tanned with Wattle Bark Extract, *ibid.*, **23**, 495-522, 1928; **26**, 143-156, 1931.

66. PICKARD, R. H., and A. E. CAUNCE: Free Acid in Leather, *J. Soc. Leather Trades Chem.*, **8**, 156, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 415, 1924.

67. PROCTER, H. R.: "Leather Industries Laboratory Book," 2d ed. 355-373, E. and F. N. Spon, London and New York, 1908; "Leather Chemists' Pocket Book," E. and F. N. Spon, London and New York, 183-198, 1912.

68. REED, H. C., and J. B. CHURCHILL: Extractor for Water-soluble Matter in Leather, *J. Am. Leather Chem. Assoc.*, **14**, 133-140, 1919.

69. REHBEIN, G.: Micro-Kjeldahl Method for Determining Nitrogen in Leather, *Collegium*, 256, 1923; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 220, 1924.

70. REITHOF, O., and C. T. GAYLEY: Determination of Ash in Leather, *J. Am. Leather Chem. Assoc.*, **13**, 7-9, 1918.

71. ROGERS, J. S.: Determination of Acid in Leather, Committee Report, *ibid.*, **13**, 319-334, 1918; **17**, 204-206, 1922; **18**, 430-438, 1923.

72. ROGERS, J. S.: Determination of Glucose in Leather, Committee Report, *ibid.*, **16**, 480-484, 1921.

73. SCALES, F. M., and A. P. HARRISON: Boric Acid Modification of the Kjeldahl Method, *Ind. Eng. Chem.*, **12**, 350, 1920.

74. SCHIAPARELLI, C., and L. CAREGGIO: Temperature of Gelatinization (T_g) and its Application to the Study of Tanning by the One-bath Chrome Process, *Boll. Ufficiale Staz. sper. ind. pelli mat. concieri.*, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 747, 1924; *Cuir tech.*, **14**, 68, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 616, 1925.

75. SCHULTZ, G. W., *et al.*: Determination of Water Solubles in Leather, Committee Report, *J. Am. Leather Chem. Assoc.*, **17**, 220-242, 1922; **18**, 254-262, 1923.

76. SEEL, E., and A. SANDER: Chemical and Microscopical Examination of Leather, *Zeit. Angew. Chem.*, **29**, I, 325-326, 333-334, 1916.

77. SELTZER, J. M.: Total, Soluble, and Insoluble Ash in Leather, Committee Report, *J. Am. Leather Chem. Assoc.*, **14**, 243-255, 1919.

78. SMALL, F. H., *et al.*: Sampling of Leather and Its Preparation for Analysis, Committee Report, *ibid.*, **16**, 394-430, 1921.

79. STACEY, L. E., *et al.*: Determination of Free Sulfuric Acid in Vegetable-tanned Leather, Committee Report, *ibid.*, **19**, 506-520, 1924.

80. SWEDISH Specifications for, and Methods of Testing Leather: *Cuir tech.*, **13**, 492, 1924; **15**, 267-271, *et seq.*, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 298, 1925; **21**, 644, 1926.

81. TERRASSE, G. L., and J. F. ANTRES: Determination of Water Solubles in Leather, Committee Report, *J. Am. Leather Chem. Assoc.*, **15**, 581-592, 1920.

82. TERROINE, E. F., G. LEPAGE, and J. PONSOT: Methods of Determining Fat in Leather, *Cuir tech.*, **15**, 260-266, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 478, 1926.

83. THOMAS, A. W.: Determination of Sulfuric Acid in Leather, *J. Am. Leather Chem. Assoc.*, **15**, 504-510, 1920.

84. THOMAS, A. W., and A. FRIEDEN: Determination of Hydrochloric Acid and Neutral Chlorides in Leather, *Ind. Eng. Chem.*, **12**, 1186, 1920.

85. U. S. Government Master Specifications: Upholstery Leather, *Bur. Stand. Circ. No. 212*, 1924; Lace Leather, *ibid.*, No. 21, 1924; Sole Leather, *Fed. Specif. Board, Specif. No. 241*; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 694, 1924; **20**, 432, 434, 1925.

86. VAN DER HOEVEN, C.: Analysis of Leather Tanned with Artificial Tannins, with Particular Reference to the Determination of Free Sulfuric Acid, *Collegium*, **251**, 281, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 127, 1925.

87. VEITCH, F. P.: Determination of Moisture in Leather, Committee Report, *J. Am. Leather Chem. Assoc.*, **17**, 262-274, 1922.

88. VEITCH, F. P., and I. D. CLARKE: Extraction of Oils and Grease from Leather, Committee Report, *ibid.*, **16**, 458-477, 1921.

89. VEITCH, F. P., and R. W. FREY: Preparation of Heavy Leather Samples for Analysis, *ibid.*, **13**, 232-239, 1918.

90. VEITCH, F. P., and R. W. FREY: Water Extraction of Leather, *ibid.*, **16**, 491-510, 1921.

91. VEITCH, F. P., and M. G. HUNT: Extraction of Leather Stuffing Oils and Greases from Sand, *ibid.*, **14**, 507-511, 1919.

92. VEITCH, F. P., and T. D. JARRELL: Determination of Moisture in Leather, *ibid.*, **20**, 334-341, 1925; **21**, 435-445, 1926; **22**, 265-274, 1927.

93. VEITCH, F. P., and T. D. JARRELL: Effect of Atmospheric Humidity on the Determination of Moisture in Leather, *ibid.*, **16**, 547-562, 1921.

94. WAGNER, J.: Determination of Chromium Content of Leather, *Collegium*, **81**, 1924.

95. WILSON, JOHN ARTHUR: "The Chemistry of Leather Manufacture," 2d ed., vol. II, The Chemical Catalog Company, Inc., New York, 1929.

96. WILSON, JOHN ARTHUR, *et al.*: Determination in Leather of Matter Extractable by Water, Committee Report, *J. Am. Leather Chem. Assoc.*, **16**, 264-280, 1921.

97. WILSON, JOHN ARTHUR, *et al.*: Extraction of Grease and Oil from Leather, Committee Report, *ibid.*, **14**, 140-178, 1919.

98. WILSON, JOHN ARTHUR, and E. J. KERN: Determination of Fat in Leather, *ibid.*, **13**, 138-141, 1917.

99. WILSON, JOHN ARTHUR, and G. O. LINES: Properties of Shoe Leather: II, Chemical Composition, *ibid.*, **21**, 198, 1926.

100. WOODROFFE, D.: Chrome Leather Analysis, III: Extraction of Oils and Fats from Chrome Leather, *J. Soc. Leather Trades Chem.*, **6**, 97, 1922; abstracted in *J. Am. Leather Chem. Assoc.*, **17**, 312, 1922; Chrome Leather Analysis, *ibid.*, **8**, 194, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 542, 1924.

101. WOODROFFE, D.: Determination of Aluminum in Chrome Leather, *J. Soc. Leather Trades Chem.*, **8**, 581, 1924.

102. WOODROFFE, D.: Determination of Fat in Leather, *ibid.*, **10**, 219, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 1081, 927; *J. Intern. Soc. Leather Trades Chem.*, **12**, 569, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 380, 1929.

103. WOODROFFE, D.: Procter-Searle Method for Determining Free Mineral Acid in Leather, *J. Intern. Soc. Leather Trades Chem.*, **11**, 394, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, **23**, 209, 1928.

104. WRIGHT, ROBERT: Determination of Moisture in Leather, Committee Report, *J. Am. Leather Chem. Assoc.*, **15**, 529-534, 1920.

CHAPTER III

MICROSCOPIC EXAMINATION OF SKIN AND LEATHER

It is extremely important for a leather chemist to know how to use the compound microscope to the best advantage and to prepare specimens of skin and leather for microscopic examination. His training should include courses in microscopy and in photomicrography. The procedure outlined in this chapter will enable a chemist without previous training in microscopy to prepare fairly satisfactory specimens for microscopic examination. He will find this very useful but should supplement the reading of this chapter by a careful study of the literature cited at the end of it.

Every leather chemist should familiarize himself with the structure of raw skin by studying it directly under the microscope. He will find the structure of skin to vary greatly, depending upon the kind of animal, its age and habits, and even upon the location on the individual creature. He should be able to correlate this structure and its variations with the functions of the skin. Training in this field will enable him to examine skin and leather more intelligently for defects and to follow the changes occurring during the conversion of skin into finished leather. Much help in this direction may be gained by a study of Chaps. II and XXXVI, Wilson's "Chemistry of Leather Manufacture" (21).

Sampling.—For vertical sections of skin or leather, it is convenient to cut specimens with heavy shears to a size of about 1 by 5 cm. For horizontal sections, the specimen may be cut 1 cm. square with shears or as a circle with a cork borer of about 1 cm. diameter. Where it is desired to study the variation in structure over the whole skin, cuttings should be made from the head, tail, shoulder, butt, backbone, belly, and fore- and hind shanks. In cutting the strips for vertical sectioning, the line of direction of the hairs should be noted. A more clearly detailed picture can usually be obtained by cutting strips so that the later sectioning can be done in definite planes, as, for example, that including a hair follicle and its *erector pili* muscle. It is important that the plane selected be kept uniform for any given series of

sections showing changes taking place during the passage of a skin through the tannery processes.

Fixing.—In studying fresh skin, in order to get sections showing the greatest detail, it is necessary to “fix” the specimen immediately after the animal has been killed. This consists in placing the specimen in some solution that will prevent a breakdown in the tissues. According to Lee (12), the word *fixing* implies two things:

. . . first, the rapid *killing* of the element, so that it may not have time to change the form it had during life, but is fixed in death in the attitude it normally had during life; and second, the *hardening* of it to such a degree as may enable it to resist without further change of form the action of the reagents with which it may subsequently be treated. *Without good fixation it is impossible to get good stains or good sections, or preparations good in any way.*

One of the most satisfactory fixing agents is Erlicki's fluid, which consists of 25 g. of potassium dichromate and 10 g. of copper sulfate dissolved in 1 l. of water. As soon as specimens of fresh skin are cut, they should be placed directly into this solution without any previous washing. The old solution should be replaced by fresh solution daily for the first 3 days and the specimens kept in the last solution until the color has completely penetrated them. For fresh calfskin, this may require from 5 to 7 days; for heavy hide, much longer. The specimens should then be washed in running tap water for 24 hr. and then dehydrated and imbedded as indicated below.

Another fixing agent that is recommended is a 10-per cent solution of formaldehyde. McLaughlin and O'Flaherty (13) found it to be rapid in its effect and without harm to the tissue structures. Daub obtained satisfactory results by fixing for 24 hr., in a mixture of 13 cc. of 40 per cent formaldehyde and 87 cc. of 3 per cent mercuric chloride solution, rinsing with water, dehydrating with increasing concentrations of alcohol, and imbedding.

Dehydrating and Imbedding.—After specimens of skin have been fixed and washed, they are ready to be dehydrated. Skins from various stages in the tannery process are dehydrated without fixing. Keep each specimen of wet skin or leather for the stated lengths of time in the following baths, using a separate bath of about 25 cc. for each specimen:

Days

1	50-per cent alcohol
1	95-per cent alcohol

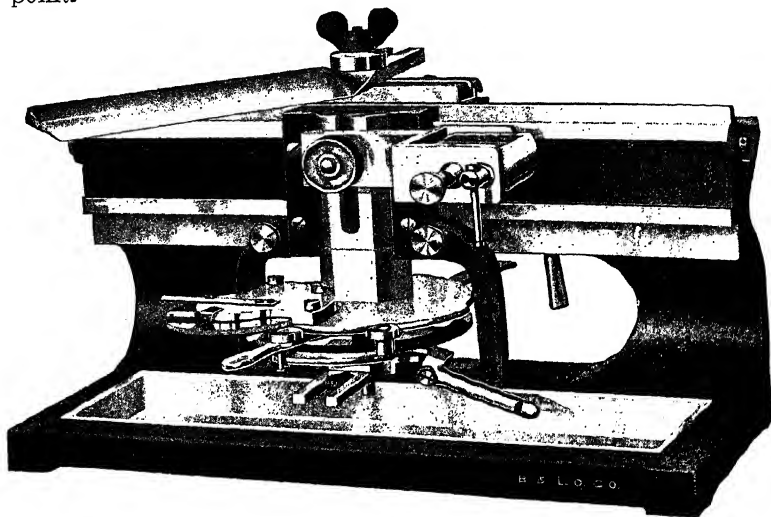
1	Absolute alcohol
1	Fresh absolute alcohol
$\frac{1}{2}$	Alcohol-xylene
$\frac{1}{2}$	Carbol-xylene
$\frac{1}{2}$	Xylene
$\frac{1}{2}$	Fresh xylene
$\frac{1}{2}$	Molten paraffin (m.p. 56°C.)

The mixture of alcohol and xylene consists of equal volumes of the two. The carbol-xylene is known as a clearing agent and has for its object the removal of any alcohol left in the specimen; it is prepared by mixing 25 cc. of molten phenol with 75 cc. of xylene. Very thick specimens may have to be left in the molten paraffin a much longer time to insure replacement of the xylene by paraffin. The paraffin is kept molten by keeping in an oven at a temperature about 5°C. above the melting point of the paraffin. Suspend each strip from the paraffin bath in an aluminum beaker having a capacity of about 100 cc., and cover with molten paraffin. Then plunge the beaker into cold water and keep there until the paraffin has completely solidified. Then heat the beaker sufficiently to allow the block to be pulled out and cut with an ordinary knife into a shape suitable for the microtome. Special molds can be purchased which are more convenient to use than the aluminum beakers; they consist of a metal plate and two metal ell's which can be pulled apart after the paraffin has solidified, leaving a block of the right size for the microtome.

When a specimen of dry leather is to be imbedded, suspend it for 1 day in a small beaker of cedarwood oil; then rinse it with xylene; then transfer it to molten paraffin, replacing with fresh paraffin each hour for 5 hr.; and then imbed as directed above.

The Microtome.—In order to prepare thin sections of skin or leather suitable for examination at high magnification, it is necessary to have a good microtome. Figure 8 shows the microtome used by the authors. It belongs to the class of instruments commonly designated as sliding block and may be moved back and forth by hand. Just below the plane swept by the knife there is a clamp which holds the object to be sectioned between movable jaws. The object clamp is attached to a frame which may be raised any distance by means of a graduated feed screw. This may be set to raise the object clamp any desired distance from 2 to 60 microns (0.002 to 0.060 mm.) with each stroke of the knife. In this way a whole series of sections of uniform

thickness can be prepared. Often it is desired to mount every section in the series so as to permit a quantitative study of the structure of a skin in three dimensions, measuring from a given point.



. S.—Automatic laboratory microtome.

Sharpening the Knife.—Without a good, sharp knife, it is not possible to get really good sections of skin or leather for study at high magnification. The utmost care and patience in sharpening microtome knives is necessary in order that they may be brought to that condition where the best results can be obtained. No matter how perfectly the microtome may be constructed, unless this detail is carefully attended to, failures are sure to follow.

If the knife has become dull or has nicks in its edge, it should first be honed on a hone of the type known to the trade as a “yellow Belgian hone”; while this type of hone cuts rapidly, it does not contain grit likely to injure the fine edge of the knife. The hone should be dressed with a lather made from palm oil soap and frequently moistened with distilled water to keep the lather from becoming too thick. Soap lather is superior to oil for honing microtome knives because it leaves the pores of the stone open, giving a quicker and cleaner cut. The knife should be passed over the stone with a free, uniform motion, without

exerting pressure other than that caused by the weight of the knife.

Figure 9 illustrates the proper movements of the knife on the hone. In honing, the edge of the knife should always be toward the direction of motion. Hone the knife on the yellow stone until all nicks are removed and a very thin wire edge appears, as can be determined by drawing the edge lightly across the thumb nail. The knife is then honed further on a hone of the type known to the trade as a "blue water hone," the surface of which is prepared by moistening and rubbing with the special rubbing stone which accompanies it. This hone is finer than the yellow

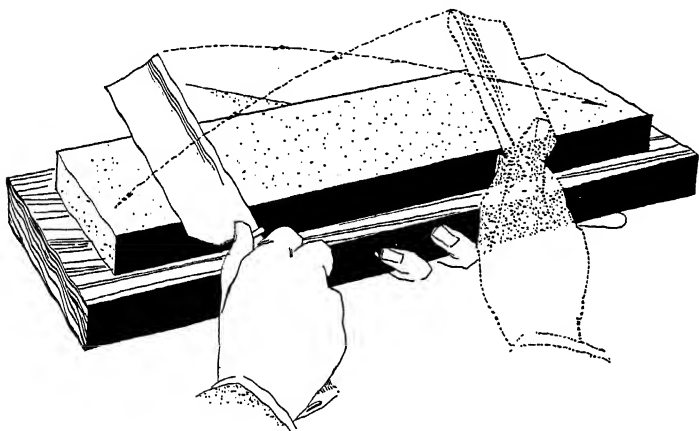


FIG. 9.—Proper movement for honing microtome knife.

stone. The knife should be moved lightly and carefully over it until a uniform keenness has been obtained along the entire edge. The quality of the edge can be judged by passing it lightly over the moistened tip of the thumb. If the feeling that the knife will enter the skin be apparent, it indicates that sufficient keenness has been obtained on the stone and the knife is ready for the strop.

In stropping, the knife edge is turned away from the direction of the stroke. Figure 10 shows the proper movement for stropping the knife, which should be allowed to pass over the strop of its own weight, as pressure is likely to round the delicate edge and destroy its uniformity. The knife should be stropped until it will cut a hair freely along its entire edge. It is then ready for

use. Skill in stropping a microtome knife cannot be acquired from a mere description. Actual practice in doing the work is absolutely necessary. The description can serve only to set the beginner on the right track.

Some microtomists finish the stropping on the palm of the hand and obtain a keenness of edge not possible in any other way known. The process is a tedious and laborious one at best, but upon it all the excellence of the finest work depends.

After a knife has been used for section cutting, it should be carefully cleaned with an old, washed-out linen cloth, being wiped from heel to point in such manner as not to touch the edge, and then carefully stropped. This stropping not only improves the edge but also coats it with some of the oil preparation in the

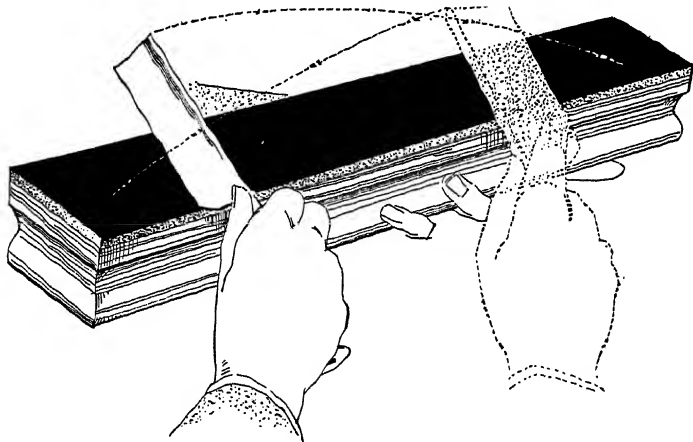


FIG. 10.—Proper movement for stropping microtome knife.

stop, thus protecting the edge and keeping it from rusting. The highly tempered steel of which these knives are made rusts very quickly, if coated with the least moisture.

One of the most satisfactory stops for microtome knives consists of a solid block of wood upon which a fine-grained piece of specially prepared leather has been stretched. It is advantageous to have one made from a piece of wood of sufficient thickness to be perfectly firm under manipulation, with prepared leather on one side and prepared canvas on the other, the canvas being used when the knife has become dull, just as in stropping a razor.

Sectioning.—Sections of leather should be cut to a thickness of less than 40 microns, if possible. Thinner sections permit higher magnifications, but they are much more difficult to produce, requiring a sharper knife and greater skill. In cutting, the section tends to curl, and great care is required to flatten it without damage.

Lay the curled section on a sheet of paper warmed from below with an electric lamp and tease with a knife to start it uncurling. Then lift it gently with forceps and place upon the surface of water at 40°C., whereupon it will flatten. Using the forceps, dip the section first into absolute methanol and then into the following mixture:

150	cc. absolute alcohol.
50	cc. ethyl ether.
2	g. dry parlodion.
2	g. Canada balsam.
1.25	g. castor oil.

Keep in this mixture only for a second and then let dry. Place the section upon a thin film of Mayer's fixative¹ on a microscope slide and press down gently, heat the slide very gradually until the paraffin melts, cool at once from this point, wash off the paraffin with xylene, then wash the section with chloroform and then with 95-per cent alcohol. If the section is to be stained, transfer it to water, giving several changes. Stain as described below, and then wash with increasing strengths of alcohol up to 95 per cent. Place a drop of santalwood oil on the section, and leave it for several hours for the solvents to evaporate. With a small pipette flood the section several times with xylene to remove the oil. Then tease away the excess of xylene from the sides of the section by means of a blotter or filter paper. Place a drop of Canada balsam on a cover glass and place over the section. Warm the slide and press gently on the cover glass, taking care not to distort the leather section, squeezing out the excess of balsam and any air bubbles. The slide is then ready for examination under the microscope or for photographing or for filing away for future reference.

Staining.—When stained with certain dyes, the different proteins of the skin assume different colors, making staining an important part of the study of raw skin. It is also valuable in photographing leather sections with the various light filters.

¹ Made by mixing equal parts of glycerin and well-beaten white of egg, adding 2 per cent of sodium salicylate, and filtering.

A great variety of stains may be employed in the study of raw skin. Only six will be described here because they have been found very useful in this kind of work. They may be prepared as follows:

1. *Van Heurck's Logwood*.—Grind 6 g. of powdered logwood extract and 18 g. of alum together in a mortar, adding 300 cc. of water very slowly. Filter and add 20 cc. of alcohol to the filtrate. Allow the solution to stand exposed to air for several weeks, adding water each day to replace that lost by evaporation. It is then ready for use. The section on the microscope slide is freed from paraffin with xylene, freed from xylene with absolute alcohol, and then treated for several minutes, successively, with the following strengths of alcohol: 95-, 75-, 50-, and 25-per cent. It is then treated with water and then with the stain for 3 min. and then rinsed with water. Where a fixative has been used, the entire slide may be dipped into the various solutions of alcohol or stain. The section is rinsed in tap water until it turns blue. After this has occurred, pass it through the series of alcoholic solutions of increasing strength. If counterstaining is to be done with the picro-indigo-carmin solution, transfer the section from the 95-per cent alcohol solution to this stain. If counterstaining is to be done with the Bismarck brown solution, transfer the section from the 95-per cent alcohol to a 0.1-per cent solution of hydrochloric acid in absolute alcohol and keep it there until it turns pink and no more color is seen to wash out. Rinse in fresh alcohol and put into the Bismarck brown stain. After staining, free the section from water with absolute alcohol and from alcohol with xylene. Then cover with a cover glass and a drop of Canada balsam.

2. *Friedlander's Logwood*.—Mix a solution of 2 g. of powdered logwood extract in 100 cc. of alcohol with a solution of 2 g. of alum in 100 cc. of water and 100 cc. of glycerin. Use like Van Heurck's stain.

3. *Picro-indigo-carmin*.—Add 1 cc. of a saturated solution of picric acid in absolute alcohol to 100 cc. of 90-per cent alcohol. Add more indigo carmin than will dissolve and let stand for several weeks, with occasional shaking. Decant, using only the clear portion. Stain section for 3 to 4 hr.

4. *Picro-red*.—To 55 cc. of a saturated solution of the dye Leather Red-X in 90-per cent alcohol add 5 cc. of a saturated solution of picric acid in absolute alcohol. Dilute with alcohol to 10 volumes before using. Allow 2 min. for staining.

5. *Weigert's Resorcin-fuchsin*.—Add 2 g. of basic fuchsin and 4 g. of resorcin to 200 cc. of water and boil for 10 min. Add 25 cc. of a 30-per cent solution of ferric chloride and boil for 5 min. longer. Then add saturated ferric chloride solution carefully until all dye is precipitated. Let stand overnight to cool and settle, decant, and discard the supernatant liquor. Dissolve the residue in 200 cc. of boiling 95-per cent alcohol and filter the hot solution into a bottle. Cool and add 5 cc. of concentrated hydrochloric acid. Dilute with an equal volume of alcohol for staining, allowing the section to remain in the dye bath for 60 to 90 min. Then rinse it with alcohol.

6. *Daub's Bismarck Brown*.—Add 5 cc. of saturated limewater to 95 cc. of absolute alcohol and then 0.25 g. of Bismarck brown-R, shake well, and

let stand for several days in contact with air, replacing any alcohol lost by evaporation. Decant and use the clear solution, keeping the section in the dye bath for one day.

Mallory and Wright (15) describe many other stains suitable for staining sections of skin. Many leather chemists will want to experiment with stains of their own.

After staining, each section must be freed from any water it may contain by rinsing in absolute alcohol. It is then rinsed with butyl alcohol and then with xylene. The sections are then covered with Canada balsam and a cover glass and are ready for examination under the microscope. When so mounted, the sections will keep indefinitely and may be filed in special cabinets holding 1,000 or more slides, which are available on the market.

Freezing Microtome.—The leather chemist may find it very desirable to have a freezing attachment for his microtome. This permits the rapid sectioning of raw skin and other tissues without



. 11.—Carbon dioxide freezing attachment.

the necessity for imbedding in paraffin, which is time consuming. Figure 11 shows a carbon dioxide freezing attachment. The flat cylinder at the top of the right end is the freezing chamber. Below and in back is a regulating valve to which is attached a copper tube which leads to a cylinder of liquefied carbon dioxide. The freezing chamber support has a clamp screw for attaching to the vertical slide of the microtome. It is customary to attach the carbon dioxide cylinder to a wall or pillar in a vertical position with the valve end down. The valve end should be somewhat higher than the freezing chamber of the microtome in order that all of the liquefied gas may run off from the cylinder freely.

The wet skin or other specimen soaked in suitable liquid is placed on the flat top of the freezing chamber. The valve of the cylinder is opened very gradually and only a small quantity of the liquid carbon dioxide is allowed to flow into the freezing chamber. If the valve is opened too wide, the carbon dioxide may freeze in the copper tube, in which case the specimen cannot

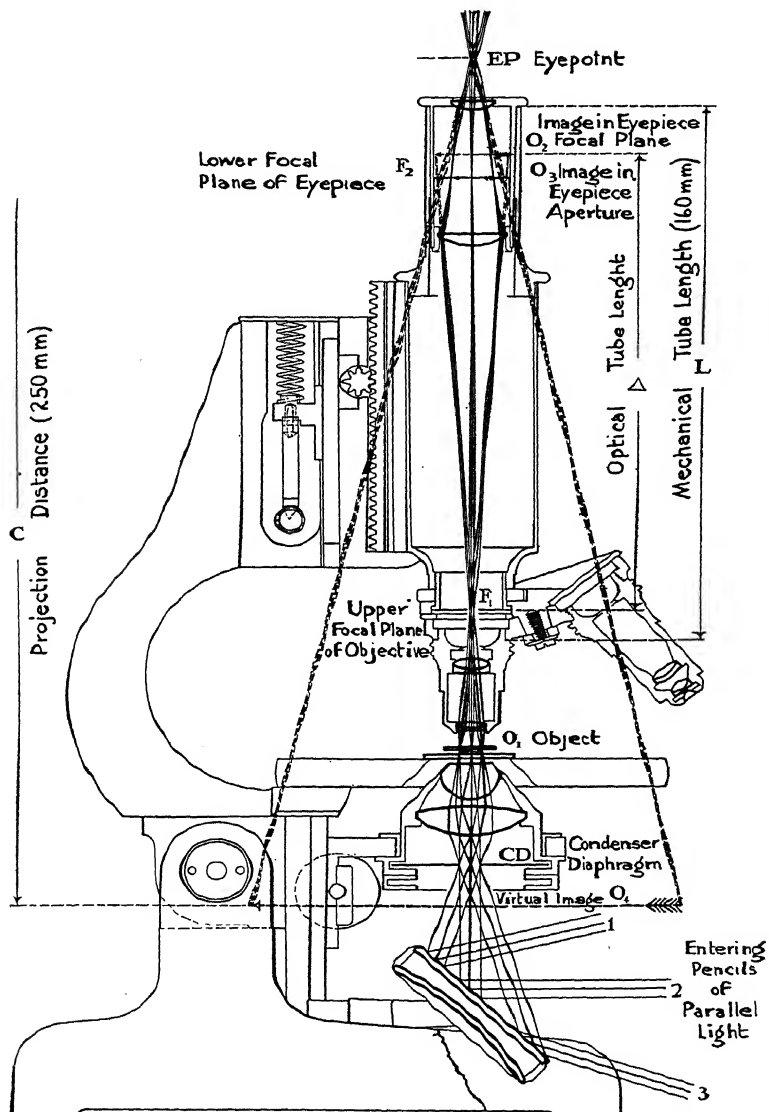
be frozen. Only a small quantity of carbon dioxide is required to freeze the specimen so that it may be sectioned in the microtome. If the specimen softens during cutting, it can be frozen again very quickly by admitting additional quantities of carbon dioxide into the freezing chamber. After the valve of the main cylinder has been opened, the regulating valve of the attachment may be used for greater precision.

The freezing method has the advantage of greater speed, but the authors have never been able to get sections with it that are so cleanly cut or that show such fineness of detail as sections obtained from specimens imbedded in paraffin. Where a special study is being made of the oily constituents of skin, the freezing method may be preferable, but the authors have found the paraffin-imbedding method much more satisfactory for ordinary studies.

The Microscope.—In order to study sections of skin and leather prepared by the methods described above, it is necessary to have a good compound microscope. It is extremely desirable, also, to know something about the structure of the microscope and how to choose the right eyepiece, objective, and condenser for any special purpose. Figure 12 shows a diagram of the path of light rays through a compound microscope. The three chief parts of the microscope are the objective, eyepiece, and substage condenser. The condenser is used to give proper illumination to transparent objects and is replaced by other forms of illuminators when opaque objects are being examined.

It will make the more detailed descriptions of the various parts of the microscope clearer, to follow, first of all, the path of light rays through the microscope as a whole. In Fig. 12 O_1 represents a tiny arrow, pointing to the right, resting on the stage between a glass microscope slide below and a cover glass above. The mirror at the bottom of the microscope is so tilted as to throw rays of light from an outside source vertically upward to the substage condenser, by which they are converged, throwing a more concentrated light upon the object. The rays of light from the illuminated arrow pass up through the series of lenses in the objective and come to a focus at O_2 in the diaphragm of the eyepiece.

If there were no eyepiece in the microscope, the image would be formed at O_2 , but the eyepiece collective lens brings this image into the diaphragm and allows the eye located at EP to see the magnified image of the object.



-Diagram showing path of light rays through compound microscope (Bausch and Lomb Optical Company).

The Objective.—The objective may be called the eye of the microscope, as on it depends the formation of the real image of the object being examined. It consists of a series of lenses suitably mounted and has two functions:

1. The formation of a magnified image of the object on the microscope stage.
2. The resolution of the details of structure of the object.

These two functions are known as magnifying power and resolving power and are dependent on the equivalent focus (e.f.) and numerical aperture (n.a.), respectively.

The magnification depends upon the distance of the image to the lens, the image distance, and the focal distance. This is illustrated for the simple convex lens in Fig. 13. The object is shown at a distance fd from the center of the lens and the real

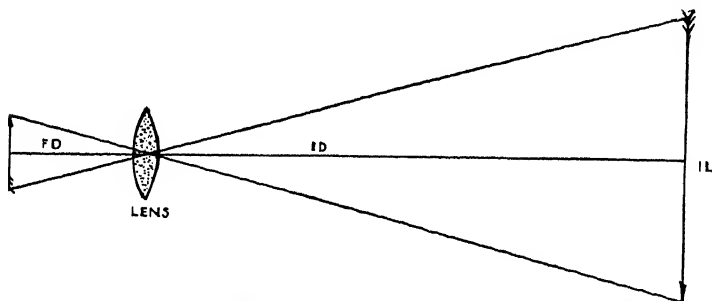


Fig. 13.—Diagram showing relation existing between the magnifying power of a simple convex lens and the ratio of image distance to focal distance. ($il/ol = id/fd$).

image at a distance of id . Taking the length of the object as ol and that of the image as il , it is apparent that the number of times the length of the object is magnified = the magnification = $il/ol = id/fd$. In other words, the magnification is equal to the image distance divided by the focal distance. If the screen receiving the image is drawn farther away from the lens, thus increasing the image distance, the image will be thrown out of focus. By shifting the position of the object or of the lens, the image can be brought back into focus; the values of both id and fd will be changed, but the above relations will still hold. With the compound microscope, increasing the image distance requires a slight movement of the microscope toward the object in order to bring the image into the sharp focus again. In evaluating

the magnifying power of an objective, it is customary to consider the image distance fixed at 250 mm. At this distance an objective having an equivalent focal length of 2 mm. would give a magnification of $250/2$ or 125 diameters, without the use of an eyepiece. The objectives which the authors have found invaluable in leather research have equivalent focal lengths of 1.9, 4, 8, 16, 32, 48, and 72 mm.

The resolving power of an objective is usually given in terms of numerical aperture. Not all of the light from a point in the object which strikes the objective lenses is effective in producing the image. If a vertical plane be passed through the center of the objective and the point in the object, then the only rays of light in this plane passing from point to objective which are effective in producing the image lie within the limits of an angle whose value is known as the angular aperture. The numerical aperture is equal to the index of refraction of the medium between the object and objective (air, water, oil, etc.) multiplied by the natural sine of one-half of this angle. The greater the numerical aperture the clearer will be the image, other things being equal. Since the objectives of shorter focus have greater magnifying power and higher numerical aperture, they are to be preferred where both high magnification and maximum resolving power are required. For practical purposes the rule may be used that the numerical aperture multiplied by 100,000 will give the number of lines per inch that can be theoretically resolved by a given objective. Objectives are usually rated according to both equivalent focal length and numerical aperture.

For precision work, one should select only objectives which have been corrected for spherical and chromatic aberration and for the cover glass placed over the section of skin or leather. In ordinary spherical lenses, there is a defect known as spherical aberration: Parallel rays at the outer edges of the lenses come to a focus nearer to the lenses than rays near the center of the lenses; instead of a single focus, a series of foci is produced and the image is blurred. A skilled lens maker overcomes this spherical aberration by the use of both convex and concave lenses made of materials of different refractive power. The concave lenses are made to have aberrations equal but opposite to those of the convex lenses. This can be done without destroying the converging action of the lenses. A similar type of aberration is produced by a cover glass; the rays of light near the outer edges

are bent more than those nearer the center. A correction for this can be made in the objective as long as the thickness of the cover glass is known. Lenses corrected for spherical aberration are known as aplanatic and the makers indicate the thickness of cover glass for which they are corrected.

Spherical aberration occurs in ordinary lenses whether one or more wave lengths of light are employed. Where white light is used, the short waves are refracted more than the longer waves, with the result that the blue-violet rays come to a focus closer to the lens than the red rays, producing a series of foci along the axis corresponding to the spectrum. This is called chromatic aberration. By combining different kinds of glass in making the lenses, differently colored rays of light can be made to come to a focus at the same point. Achromatic objectives are those whose spherical aberration has been corrected for one color and the chromatic aberration for two colors. Apochromatic objectives are those whose spherical aberration has been corrected for two colors and the chromatic aberration for three colors. These are the objectives that should be employed where it is essential to have the images of differently colored portions of the object equally sharp. Their manufacture involves the use of correcting materials other than glass, such as fluorite and fluorspar.

In order to get proper illumination for objectives of very small equivalent focal length, such as the 1.9-mm. objective, use is made of the fact that thickened cedarwood oil has practically the same index of refraction as glass. A drop of oil placed on the cover glass and the bottom lens of the objective dipped into it so that the light does not have to travel across an air field but passes from the object to the objective only through glass and oil having the same refractive index. In this way the light suffers no refraction. Objectives made for use with oil are called oil-immersion objectives.

The Eyepiece.—The eyepiece in the compound microscope consists of a series of converging lenses and its chief purpose is to act with the eye as a magnifier of the real image formed by the objective. Use is made of it also to correct some of the defects of the objective. The most common type of eyepiece is called Huygenian after its inventor, a Dutch astronomer named Huygens. It consists of a planoconvex fieldlens and a similar, but higher powered, eyelens, the convex surfaces of both facing

downward. An opaque disk with an opening in the center, called a diaphragm, is placed in the eyepiece tube at the focal point of the eyelens, which is between the two lenses.

Eyepieces are numbered according to their magnifying powers. The number 5 \times indicates that the eyepiece magnifies the real image so as to make its linear dimension five times as great.

The eyepiece is inserted in the top of the optical tube and the objective is attached to the bottom. This tube is so constructed that its length may be varied at will. For most purposes, the tube length, as shown in Fig. 12, is set at 160 mm. In photomicrography, it is desirable to know approximately what combinations of objective, eyepiece, and distance from eyepiece to ground glass are required to produce given magnifications. Table 18 gives the approximate magnifications resulting from various combinations of objectives and eyepieces when the tube length is 160 mm. and the image is projected at a distance of 250 mm. from the eyepiece. The upper number in each case is the magnification in diameters or the number by which the linear dimension has been multiplied. The lower number is the actual diameter of the field shown. The magnification for other projection distances is obtained by multiplying by the projection distance in millimeters and dividing by 250. For example, where the magnification is 15 diameters at a projection distance of 250 mm., it is 45 diameters at a projection distance of 750 mm. By initial magnification is meant that number which multiplied by the power of the eyepiece gives the total magnification of the set-up.

Micrometer Eyepiece and Use with Stage Micrometer.—Micrometers or micrometer scales are used for measuring the actual size of the objects being examined under a microscope. Two kinds are generally employed, the stage micrometer and the eyepiece micrometer. The usual stage micrometer consists of a glass slide 75 by 25 mm. with 2 mm. divided in tenths by parallel lines. Two of the spaces are again divided in tenths, making 20 spaces each equal to 0.01 mm. The lines are ruled directly on the slide surface and protected by a thin cover glass cemented over the ruled area.

The eyepiece micrometer is a glass disk upon which is ruled a series of lines bounding spaces. The number of divisions is immaterial and, within certain limitations, also the distance between the lines, since the value of this distance must first be

TABLE 18.—MAGNIFICATIONS AND REAL FIELDS
 Tube length = 160 mm.; projection distance = 250 mm.

Equivalent focal length of objective, millimeters	Initial linear magnification	Achromatic and fluorite objectives and Huygenian eyepieces					
		5	6.4	7.5	10	12.5	15
48	2.0	10.90 mm. 13.0	9.5 mm. 16.6	9.25 mm. 19	7.7 mm. 26	7.5 mm. 32	5.82 mm. 39
40	2.6	8.4 mm. 20	7.3 mm. 26	7.1 mm. 30	5.9 mm. 40	5.75 mm. 50	4.5 mm. 60
32	4.0	5.7 mm. 50	4.9 mm. 64	4.75 mm. 75	3.9 mm. 100	3.8 mm. 125	3.0 mm. 150
16	10.0	2.19 mm. 105	1.91 mm. 134	1.82 mm. 157	1.49 mm. 210	1.49 mm. 263	1.15 mm. 315
8	21.0	1.09 mm. 215	0.95 mm. 276	0.90 mm. 320	0.71 mm. 430	0.71 mm. 537	0.57 mm. 645
4	43.0	0.53 mm. 225	0.45 mm. 288	0.43 mm. 338	0.35 mm. 450	0.35 mm. 562	0.27 mm. 675
4	45.0	0.51 mm. 300	0.44 mm. 384	0.42 mm. 450	0.33 mm. 600	0.33 mm. 750	0.27 mm. 900
3	60.0	0.37 mm. 485	0.33 mm. 621	0.31 mm. 727	0.25 mm. 970	0.25 mm. 1,212	0.20 mm. 1,455
1.9	97.0	0.24 mm. 500	0.21 mm. 640	0.20 mm. 750	0.16 mm. 1,000	0.16 mm. 1,250	0.125 mm. 1,500
1.8	100.0	0.23 mm. 500	0.20 mm. 640	0.19 mm. 750	0.15 mm. 1,000	0.15 mm. 1,250	0.12 mm. 1,500

Achromatic and fluorite objectives and hyperplane eyepieces							
		5	7.5	10	12.5	15	20
16	10	50 mm. 2.26 mm.	75 mm. 1.88 mm.	100 mm. 1.74 mm.	125 mm. 1.42 mm.	150 mm. 1.20 mm.	200 mm. 0.90 mm.
8	21	105 mm. 1.05 mm.	157 mm. 0.88 mm.	210 mm. 0.81 mm.	263 mm. 0.66 mm.	315 mm. 0.55 mm.	420 mm. 0.41 mm.
4	43	215 mm. 0.52 mm.	323 mm. 0.44 mm.	430 mm. 0.41 mm.	537 mm. 0.34 mm.	645 mm. 0.28 mm.	800 mm. 0.21 mm.
4	45	225 mm. 0.51 mm.	338 mm. 0.43 mm.	450 mm. 0.40 mm.	562 mm. 0.33 mm.	675 mm. 0.27 mm.	900 mm. 0.20 mm.
3	60	300 mm. 0.37 mm.	450 mm. 0.32 mm.	600 mm. 0.29 mm.	750 mm. 0.24 mm.	900 mm. 0.20 mm.	1,200 mm. 0.15 mm.
1.9	97	485 mm. 0.23 mm.	727 mm. 0.20 mm.	970 mm. 0.18 mm.	1,212 mm. 0.15 mm.	1,455 mm. 0.12 mm.	1,940 mm. 0.09 mm.
1.8	100	500 mm. 0.22 mm.	750 mm. 0.19 mm.	1,000 mm. 0.17 mm.	1,250 mm. 0.14 mm.	1,500 mm. 0.11 mm.	2,000 mm. 0.08 mm.

Apochromatic objectives and compensating eyepieces							
		5	7.5	10	12.5	15	25
16	10	50 mm. 2.35 mm.	75 mm. 2.00 mm.	100 mm. 1.30 mm.	125 mm. 1.30 mm.	150 mm. 1.10 mm.	250 mm. 0.71 mm.
8	20	100 mm. 1.12 mm.	150 mm. 0.94 mm.	200 mm. 0.63 mm.	250 mm. 0.63 mm.	300 mm. 0.53 mm.	500 mm. 0.342 mm.
4	45	225 mm. 0.49 mm.	338 mm. 0.43 mm.	450 mm. 0.28 mm.	562 mm. 0.28 mm.	675 mm. 0.23 mm.	1,125 mm. 0.141 mm.
3	62	310 mm. 0.358 mm.	465 mm. 0.302 mm.	620 mm. 0.201 mm.	775 mm. 0.201 mm.	930 mm. 0.165 mm.	1,550 mm. 0.109 mm.
3	61	305 mm. 0.375 mm.	457 mm. 0.315 mm.	610 mm. 0.21 mm.	762 mm. 0.21 mm.	915 mm. 0.175 mm.	1,525 mm. 0.11 mm.
1.9	90	450 mm. 0.247 mm.	675 mm. 0.208 mm.	900 mm. 0.139 mm.	1,125 mm. 0.139 mm.	1,350 mm. 0.114 mm.	2,250 mm. 0.075 mm.

(R. F. = diameter of real field in millimeters. Magnification for any projection distance can be calculated by multiplying by the projection distance in millimeters and dividing by 250. Magnification for a 25× eyepiece is just twice that for the 12.5× eyepiece. Real fields are only approximate and vary with the method of construction of the lenses.)

determined in terms of the known values of the spaces on the stage micrometer.

The eyepiece micrometer rests upon the diaphragm of the eyepiece. The eyelens is removed and the micrometer inserted ruled surface downward. The eyelens is replaced and the eyepiece is inserted in the microscope. If the lines of the scales do not appear distinctly when looking into the eyepiece, the eyelens must be unscrewed to the extent necessary to bring the scale into exact focus.

In determining the measuring value of the eyepiece micrometer, the stage micrometer is placed in focus on the stage. It is known that the value of its spaces is 0.1 or 0.01 mm. By looking into the microscope with both eyepiece and stage micrometers in place, the position of the stage micrometer can shift so that one line of the eyepiece micrometer is in exact coincidence with one line of the stage micrometer. It will then be seen that a certain number of eyepiece spaces are contained within one or more spaces on the stage micrometer. It will be noted, for example, that 13 spaces of the eyepiece micrometer cover a distance equal to 2 spaces on the stage or 0.2 mm. One space of the eyepiece micrometer thus covers a length of $0.2/13$ or 0.0154 mm. on the slide. The value of the space on the eyepiece micrometer will vary according to the power of the objective, the power of the eyepiece, and the tube length or distance between eyepiece and objective. The usual tube length is 160 mm., and this is generally engraved on microscopes having draw tubes. The value of each space of the eyepiece micrometer having been determined, the stage micrometer is laid aside and the eyepiece micrometer used alone for the direct measurement of the size of the object placed under the microscope objective.

Compensating Eyepieces.—A compensating eyepiece, as the name implies, compensates for the residual errors in the apochromatic objectives. In the case of apochromatic objectives, although the differently colored images of the object lie in the same plane, they are of different sizes. With ordinary eyepieces, this causes the appearance of color fringes in the margin of the field. The compensating eyepiece is so constructed as to neutralize this effect. A combination of apochromatic objective and compensating eyepiece gives a field free from color to the very margin. Compensating eyepieces also work very well with achromatic objectives whose focal length is 8 mm. or less but are not satisfactory when used with lower powers.

Flat-field Eyepieces.—Flat-field eyepieces, sometimes called “hyperplane,” present a flatter image plane than Huygenian eyepieces, which allows a larger field of view well adapted for photomicrography. They effect a compensation about halfway between the Huygenian and compensating eyepieces. This makes their use with high-power achromatic objectives, fluorite, and apochromatic objectives extremely advantageous.

The Substage Condenser.—The purpose of the substage condenser is not only to condense light, thus giving an amply illuminated field when the illumination would otherwise be insufficient, but also and more especially to illuminate the object with a cone of light having an angular aperture equal to that of

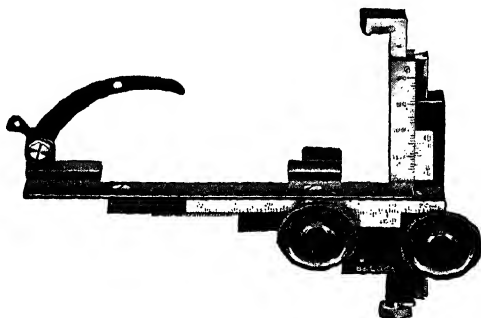


FIG. 14.—A mechanical stage.

the objective, which is absolutely unattainable with a mirror only, as well as to provide means for controlling the amount and character of the illumination to suit the various conditions of work.

The ordinary Abbe condensers are neither chromatically nor spherically corrected but serve their purpose very well for all ordinary work. Their function is to send light through the object under an angle sufficiently large to fill the aperture of the objective with light. They are available in two numerical apertures: 1.20, containing two lenses with top lens removable; and 1.40, containing three lenses. The condenser mounts fit into the substage from below and are provided with an iris diaphragm, which controls the amount of light entering the condenser and the angle of the emitted cone. They are also provided with a carrier for holding a blue-glass disk or a dark-ground stop.

Mechanical Stage.—For routine examinations of skin and leather sections under the microscope, a mechanical stage is invaluable. The form in common use is made to attach to the right-hand edge of the microscope stage and offers the convenience of complete removal when not desired for use. It

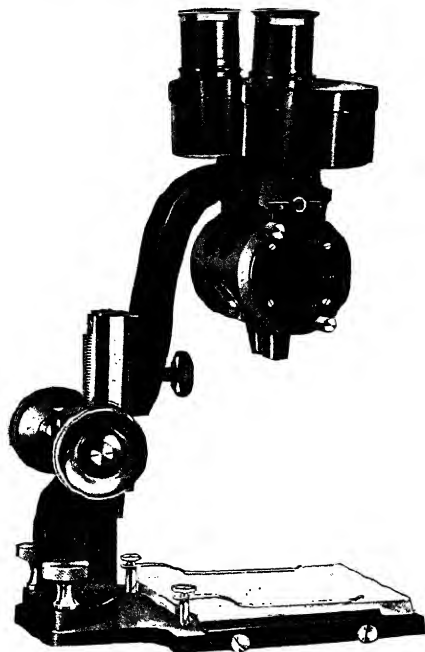


FIG. 15.—Binocular wide-field microscope.

provides for methodical examination of an object under the microscope with the assurance that every portion of it has been covered and with a degree of comfort which must be experienced to be appreciated. Movement of the specimen is by rack-and-pinion adjustment in two directions at right angles to each other. The right-and-left movement covers 75 mm. and the forward-and-back movement 40 mm. Figure 14 shows a typical mechanical stage.

The stage pictured is provided with scales in single millimeters with vernier reading to tenths. This makes it possible to record

the exact position of some point in the specimen, which may then be located later at will. The stage is provided with a slide holder to hold the slide firmly in place.

Binocular Wide-field Microscope.—Few recent developments in the microscope have proved as useful to the tanner as the new binocular wide-field microscope. It can be used to great advantage in examining the grain surface of whole skins without in any way damaging them. A convenient type is shown in Fig. 15.

The wide-field microscope is of the Greenough binocular type with modification of the angle of vision permitting long periods of observation with a minimum of eye strain due to overconvergence. The body tube is double or a combination of two microscope tubes with upper parts fitted with Porro prisms permanently set in place but rotatable by their mounts for adjusting position of eyepieces to the observer's pupillary distance. One image merges with the other, and the specimen is seen stereoscopically, erect and not transposed, which is not the case in the ordinary microscope, where the image is reversed and inverted. Eyepieces are of high optical correction to secure at the same time wide angle of view, high eye point, and proper definition over the field-of-view area. Three pairs of objectives, each pair of different power, are mounted in a nosepiece which can be revolved vertically, permitting rapid shift from one power to another.

References

1. BECK, C.: "The Microscope," R. & J. Beck, Ltd., London, 1924.
2. BOULANGER, H.: Micrographic Study of Leather, *Bull. Soc. d'Encouragement pour l'Industrie Nationale*, February, 1908.
3. BOULANGER, H.: Microscopic Examination of Leather, *Rev. d'Artillerie*, tome 74, 1909.
4. CHAMOT, E. M.: "Elementary Chemical Microscopy," John Wiley & Sons, Inc., New York, 1916.
5. COLES, A. C.: "Critical Microscopy," J. & A. Churchill, London, 1921.
6. GAGE, S. H.: "The Microscope," 12th ed., Comstock Publishing Co., Ithaca, N. Y., 1917.
7. GAGE, S. H., and H. P. GAGE: "Optic Projection," Comstock Publishing Co., Ithaca, N. Y., 1914.
8. HANAUSEK, T. F.: "The Microscopy of Technical Products." English trans. by A. L. Winton, John Wiley & Sons, Inc., New York, 1916.
9. HIND, H. L., and W. B. RANGLES: "Handbook of Photomicrography," E. P. Dutton & Company, New York, 1927.
10. KAYE, M., and D. J. LLOYD: A Histological and Physico-chemical Investigation of the Swelling of a Fibrous Tissue, *Proc. Royal Soc., B*, **96**, 293, 1924.

11. KUNTZEL, A.: "Histology of Animal Skin," Theodor Steinkopff, Dresden and Leipzig, 1925.
12. LEE, A. B.: "The Microtometist's Vade Mecum," 8th ed., P. Blakiston's Son & Co., Philadelphia, 1921.
13. McLAUGHLIN, G. D., and F. O'FLAHERTY: Micro-tannology, *J. Am. Leather Chem. Assoc.*, **21**, 338, 1926.
14. MALLORY, F. B.: "The Principles of Pathologic Histology," W. B. Saunders Co., Philadelphia, 1923.
15. MALLORY, F. B., and J. H. WRIGHT: "Pathological Technique," 8th ed., W. B. Saunders Co., Philadelphia, 1924.
16. SEYMOUR-JONES, A.: Physiology of Skin, *J. Soc. Leather Trades Chem.*, serially 1917-1921.
17. SHEPPARD, S. E., G. H. RODMAN, *et al.*: "Photography as a Scientific Instrument," D. Van Nostrand Company, Inc., New York, 1923.
18. TURLEY, H. G.: Chemico-histological Study of Leather Manufacture, *J. Am. Leather Chem. Assoc.*, **21**, 117, 1926.
19. WHIPPLE, G. C.: "The Microscopy of Drinking Water," 4th ed., John Wiley & Sons, Inc., New York, 1928.
20. WIGHTMAN, E. P., and A. P. H. TRIVELLI: Photography through the Microscope, *The American Annual of Photography*, 1928.
21. WILSON, J. A.: "The Chemistry of Leather Manufacture," 2d ed., vol. I, 1928; vol. II, 1929, The Chemical Catalog Company, Inc., New York.
22. WILSON, J. A., and G. DAUB: Properties of Shoe Leather: I, Micro-structure, *J. Am. Leather Chem. Assoc.*, **21**, 193, 1926.

CHAPTER IV

PHYSICAL PROPERTIES OF LEATHER

Quantitative measurements of the physical properties of leather are greatly complicated by its heterogeneous structure. The value of a given property may vary so greatly over the area of a skin as to make any single measurement meaningless unless the location of the part tested is accurately defined. Some properties are very sensitive to variations in the tannery processes. The tensile strength, for example, is greatly affected by the degree to which the leather may be split (52); the ventilating properties are markedly affected by the finishing materials used (56); and the area change of the finished leather with relative humidity of the atmosphere is dependent upon the kind of tannage (53). Some properties of leather are not well defined, and the value of a skin may be determined by an expert appraiser who cannot describe to the layman just what he feels or sees in the leather that is responsible for his appraisal. Many makers and users of leather still rely upon the qualitative observations of men experienced in handling leather, although quantitative methods for evaluating the physical properties of leather are being developed rapidly. Many of these quantitative methods furnish information that could not possibly be gained from the mere appearance or feel of the leather and so are being used to an increasing extent to supplement the findings of the qualitative observers.

STRENGTH AND STRETCH

The tensile strength of leather and its resistance to stretching are usually measured at the same time. If a strip of leather of uniform cross-section be suspended from a rigid support and weights be applied to the lower end by means of a clamp with a pan to hold the weights, it will be found that the strip will increase in length as more weights are added until the leather breaks. The percentage increase in length at any point is known as the *stretch* and the weight required to break the leather is known as the

strength. The tensile strength of a strip of leather is defined as the weight per unit area of cross-section required to break the strip.

Measurements of strength and stretch are usually made on machines designed especially for the purpose. Figure 16 shows the type of machine used by the authors. The leather to be tested is cut with a die to a rectangle 1 by 6 in. Its average thickness is measured by means of a sensitive thickness gage and the area of the cross-section calculated. If the thickness of the strip is 0.075 in., the area of the cross-section is 0.075 sq. in., or 0.48387 sq. cm. The strip is clamped into place with the two clamps shown at about the middle of the machine. These are spaced 4 in. apart, leaving 1 in. of the leather in each clamp to insure its holding tightly. The upper clamp is suspended from the short arm of a lever, the other end of which is loaded with a heavy weight. As the leather is pulled down, the weight arm is raised and a scale records the load on the leather. The lower clamp is gradually pulled down by means of an electric motor with gear and screw connections. As the leather is pulled down, the load upon it increases and may be read off from the scale. When the leather breaks, the weight arm does not drop but is held in place by cogs. The load required to break the strip may then be read from the scale.

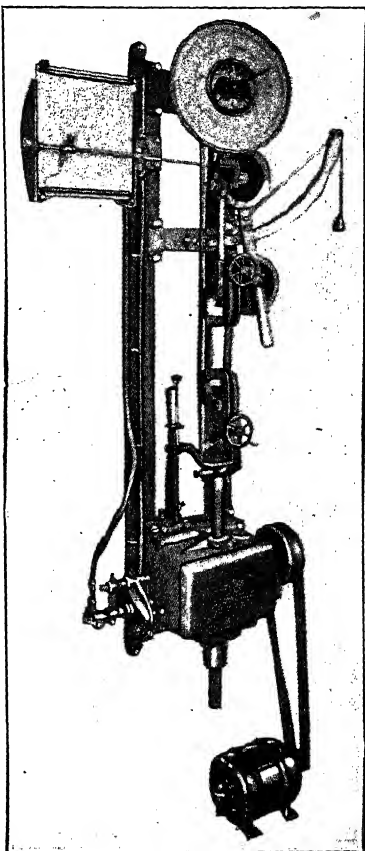


FIG. 16.—Vertical machine for measuring strength and stretch of leather.

Attached to the upper left-hand side of the machine, there is a recorder which draws on a chart with ink a curve showing the stretch of the leather as a function of load up to the breaking point. Figure 17 shows the recording mechanism more clearly. The vertical scale gives the increase in length of the strip and the horizontal scale the load in pounds. If the stretch for a given

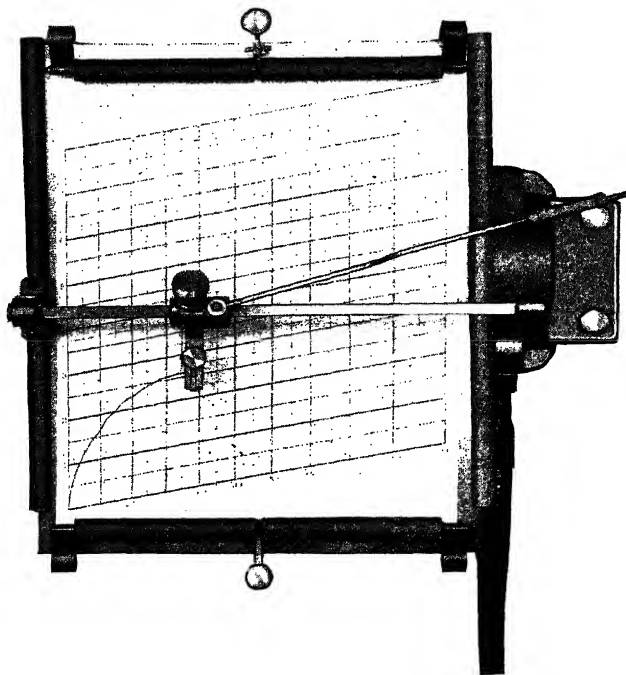


FIG. 17.—Autographic recorder.

load is 1 in., the percentage stretch is 25, since the initial distance between the jaws of the clamps was 4 in. At this point, the jaws are 5 in. apart. The strips to be tested may, of course, be cut to any desired length or width and the jaws set any desired distance apart, within limits. Figure 18 shows a machine of the horizontal type, which may be found more convenient for heavy leathers of very high tensile strength.

Effect of Location.—When taking a sample of leather for measuring strength and stretch, it is necessary to define the

location upon the skin accurately. Figure 19 shows how the strength and stretch varied over the area of a typical vegetable-tanned calfskin (44). Each rectangle shows the location of a strip 1 by 6 in. In each rectangle, the number to the left is the thickness of the strip in millimeters, the middle number is the tensile strength in kilograms per square centimeter cross-section, and the number to the right is the percentage stretch under a load of 225 kg. per square centimeter of cross-section. Figure 20

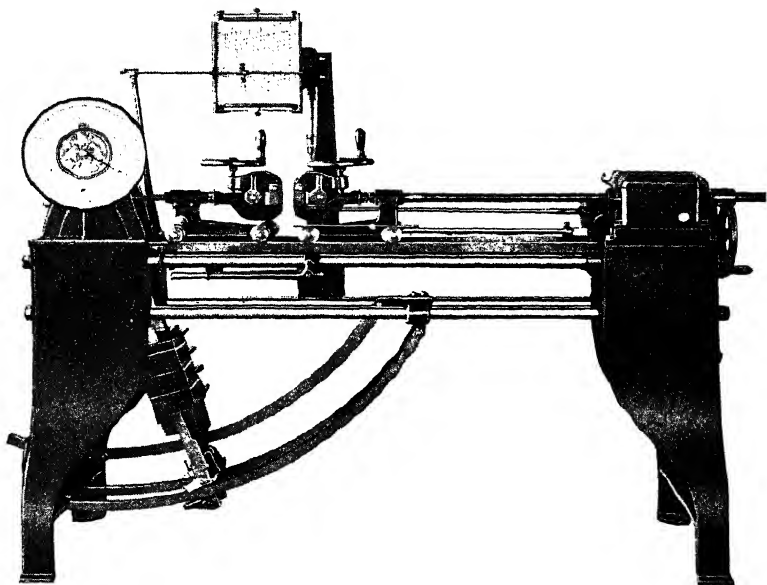


FIG. 18.—Horizontal machine for measuring strength and stretch of leather.

was prepared from tests made on a number of typical calfskins, both chrome and vegetable tanned (41). It shows more graphically how the strength and stretch vary over the area of a typical calfskin.

This variation makes sampling rather difficult. For routine measurements of calfskins, the authors cut three 1- by 6-in. strips, with their lengths parallel to the line of the backbone and about 6 in. from it. The middle strip is cut with its ends equidistant from the head and tail ends of the skin and the other two strips with their ends about 1 in. from the middle strip.

The measurements of all three strips are recorded separately. Together, they furnish reliable information as to the strength and stretch of the skin. The establishment of any routine testing should be preceded by a series of tests covering the entire areas of skins of each kind included in the routine measurements.

Effect of Relative Humidity (38, 54).—The tensile strength of chrome leathers not having a high fat content varies greatly with

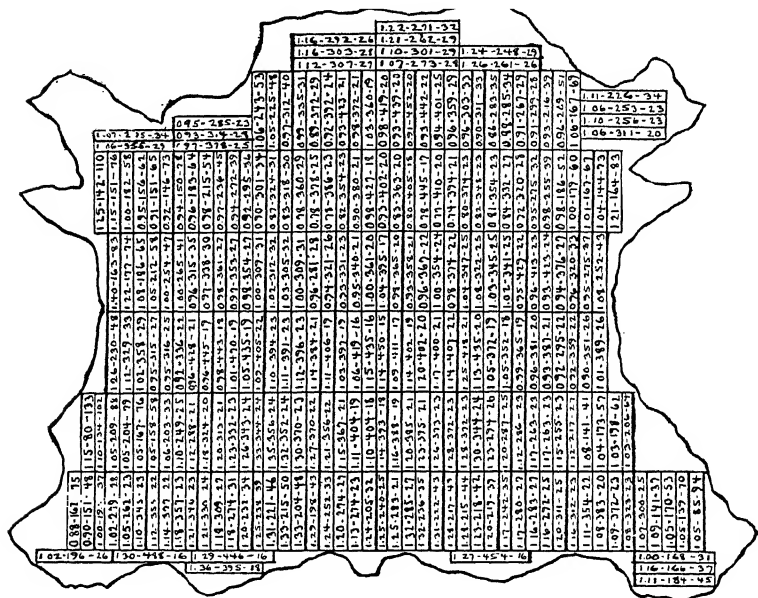


FIG. 19.—Chart showing variation in thickness, strength, and stretch of typical vegetable-tanned calf leather over the entire area of the skin. Test strips cut 1 by 6 in. in the positions indicated. In each strip, the number to the left is the thickness of the strip in millimeters; the middle number is the tensile strength in kilograms per square centimeter; and the number to the right is the percentage stretch under a load of 225 kg. per square centimeter cross-section.

the relative humidity of the atmosphere because of the changes in water content which such leathers undergo. When chrome calf leather at 50 per cent relative humidity is brought into equilibrium with a dry atmosphere, it may lose as much as 30 per cent of its tensile strength; at 100 per cent relative humidity, it may gain 30 per cent in strength. Vegetable-tanned leathers, which normally are of relatively high fat content, are but little

affected by changes in relative humidity. In sampling leathers that are much affected by change in relative humidity, pieces larger than 1 by 6 in. should be cut and placed in air-tight containers over 11.8-normal sulfuric acid, which tends to maintain a relative humidity of 50 per cent in the atmosphere above (57). For still greater precision, the containers should be placed in constant-temperature baths. Where accurate comparisons are desired, all measurements should be made on strips in equilibrium with air at 50 per cent relative humidity and at 25°C.

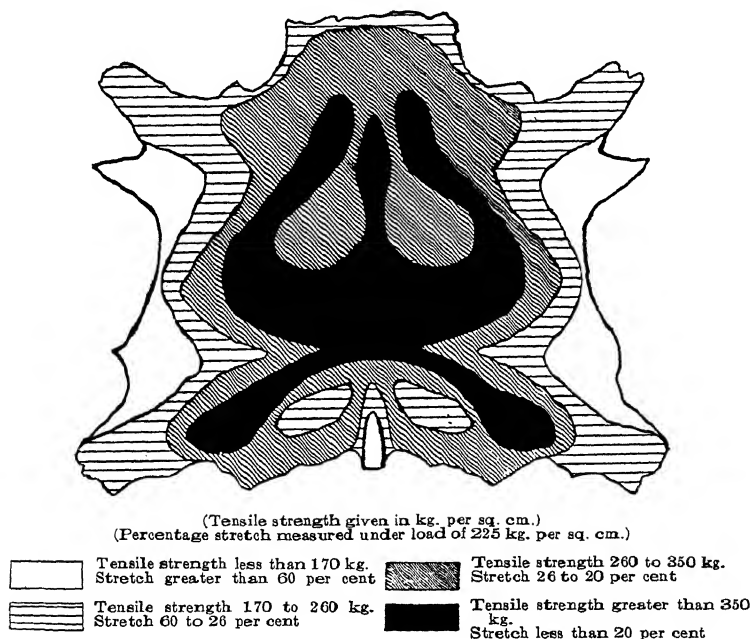


FIG. 20.—Chart showing variation in strength and stretch of calf leather over the entire area of a skin.

Making the Determination.—Cut a rectangular strip from the desired location on the skin when in equilibrium with an atmosphere of about 50 per cent relative humidity. The strip may be cut any desired size, but the authors prefer one 1 by 6 in. in their work on calf leathers. With a sensitive thickness gage, measure the thickness of the strip at five points spaced equally but not including 1 in. at each end. The average of these is taken as the average thickness. Since the strip is 2.54 cm. wide, the area of the

cross-section is taken as 2.54 times the average thickness in centimeters. Measurements of cross-section should be accurate to 0.0001 sq. cm. Set the scale reading of the machine at zero and the pen of the recorder at the origin of the chart. With the jaws of the clamps set 4 in. apart, insert the strip of leather, clamping tightly to prevent any slipping. If the leather

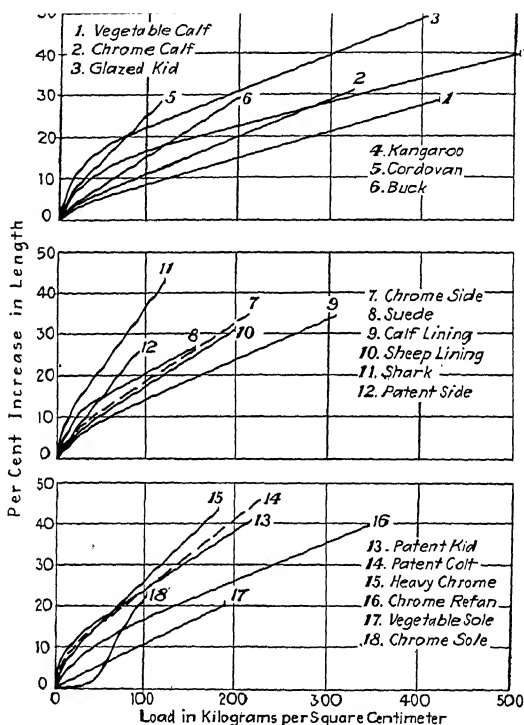


FIG. 21.—Stretch of various leathers as a function of load per unit width. The endpoint of each curve is the breaking point and a measure of strength. Each curve represents the average of triplicate measurements.

is too strong for the clamps to hold, cut another strip only half as wide for the test. Start the motor running and the recorder will plot the stretch as a function of the load, and the end point gives the breaking load.

The chart gives the load applied to 1 in. width, and from this calculations must be made to get the load per square centimeter of cross-section. Figure 21 (46) shows several charts replotted to give the load in kilograms and the stretch as increase in length of the strips. The 18 leathers represented are those whose

chemical analyses are given in Table 6 of Chap. II. The end points give the load in kilograms required to break a strip 1 in. wide. Figure 22 gives the same information but in terms of unit cross-section of the leather. In making the calculations, only the initial cross-sections are considered. Actually, the cross-section decreases as the leather is stretched, but it appears to be the initial measurements that are important.

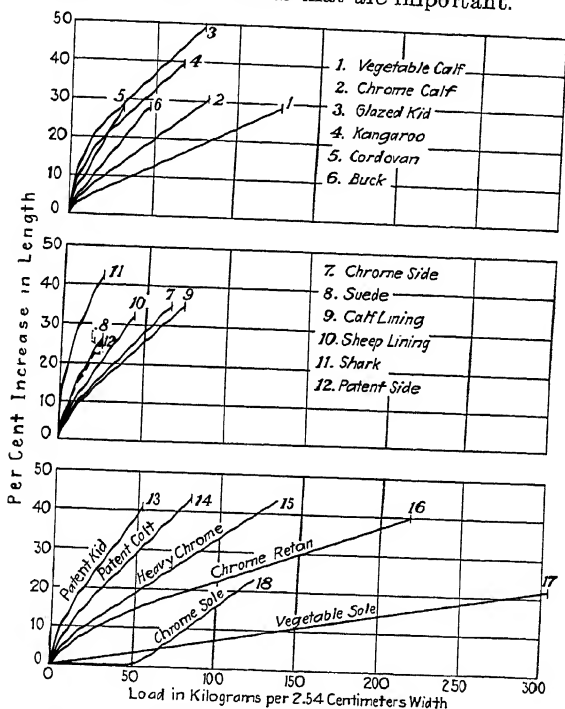


FIG. 22.—Stretch of various leathers as a function of load per unit area of cross-section. The end-point of each curve represents the tensile strength. Each curve gives the average of triplicate measurements.

In comparing different leathers, it is desirable to compare percentage of stretch under a constant load, rather than under the breaking load, which varies from leather to leather. For calf leathers, this arbitrarily chosen load may be 225 kgm. per square centimeter, which is less than the usual breaking load for this kind of leather. To obtain from the chart the stretch

corresponding to this load, divide the observed breaking load (in kilograms) by the calculated breaking load per square centimeter, and multiply by 225. The product is the actual applied load in kilograms equivalent to an applied load of 225 kgm. per square centimeter. Read from the chart the stretch in inches corresponding to this load, divide by the initial length in inches, and report percentage of stretch at 225 kgm. per square centimeter.

Method for Determining Effect of Variable Factors upon Strength and Stretch.—The wide variation of strength and

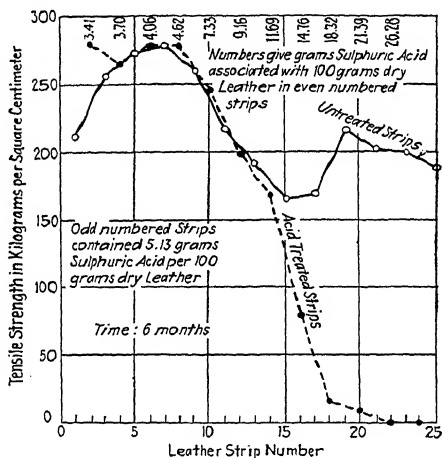


FIG. 23.—Illustrating method used to determine effect of variable factors upon tensile strength.

stretch over the area of a skin complicates any tests made to determine the effect of any special treatment upon these properties, because any strips being compared after different treatments may actually have had very different strengths before the treatment was made. In studying the effect of sulfuric acid upon the tensile strength of leather, Wilson (43) overcame this difficulty by selecting areas of leather which could be cut into series of strips such that the curve for variation in strength from one end to the other could be obtained simply by testing every other strip. If the odd-numbered strips were used to get the curve, the strength of the even-numbered strips could be obtained from the curve without the necessity for actually breaking them. The

even-numbered strips could then be used for experiments and their loss in strength measured after any special treatment. It is further possible to reduce errors to a very small value by running duplicate or triplicate series.

The method is illustrated for a concrete case in Fig. 23. A piece of finished chrome calf leather, 75 by 17 cm., was cut into 25 strips, each 3 by 17 cm., numbered from 1 to 25. The odd-numbered ones were cut with the die into strips 1 by 6 in. and measured at once for tensile strength. The even-numbered ones were wet with solutions of different pH value ranging from half-normal sodium bicarbonate to five-normal sulfuric acid. The sodium bicarbonate solutions were used to get strips of leather containing less than the usual amount of sulfuric acid. The strips were blotted, air-dried, and kept for 6 months to age. Then their tensile strengths were measured and plotted along with those for the untreated strips in Fig. 23. The broken strip in each test was analyzed for water and sulfuric acid; the latter value is recorded on the graph.

Up to an acid content of about 10 per cent, the two curves practically coincide, but they diverge sharply with further increase in acid content, the acid-treated pieces finally losing all measurable strength. The distance between the two curves gives a measure of the progressive loss of strength with increasing acid content of the leather. For example, take strip No. 16 with a tensile strength of 79. A line drawn directly upward to the curve for the untreated strips intersects it at the value 168, which may be taken as the strength of No. 16 before the acid treatment and aging. We may, therefore, conclude that the treatment has caused the leather to suffer a loss of 53 per cent in strength. This procedure makes it possible to determine the percentage loss in strength of leather resulting from any special treatment. The effect upon stretch can, of course, be determined at the same time.

Effect of Splitting.—In making measurements of the tensile strength of light leathers, it is extremely important to appreciate how very greatly the strength is reduced by splitting or reducing the thickness of the leather in any way. Wilson and Kern used the method just described to determine the effect of splitting calf leather upon its strength and stretch. Figure 24 shows the effect of splitting upon the strength of a chrome-tanned calfskin. The alternate strips of leather used for the test were split into

two layers on a band-knife machine and each strip was broken separately.

Splitting of light leathers always causes a loss in strength per unit width and the sum of the strengths of the two splits is always less than the strength of the unsplit strip. This is shown by the uppermost curve in Fig. 24. The distance of this curve from the 100 line gives the total loss in strength of the leather due to splitting. When this leather was split into two layers of equal thickness, the grain layer was found to be only 26 and the flesh layer only 16 per cent as strong as the unsplit leather, making a

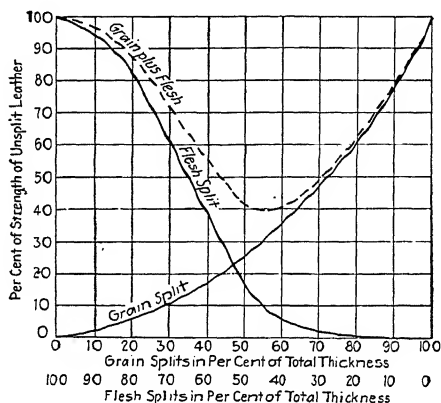


FIG. 24.—Effect of splitting upon the tensile strength of chrome calf leather. The strength of the split is given in terms of the whole leather. The strength is calculated per unit width, not cross-section. Average tensile strength of the leather tested was 258 kg. per square centimeter. Average thickness was 1.04 mm.

total loss in strength due to splitting of 58 per cent. On the other hand, when 1- by 6-in. strip was cut into two strips each $\frac{1}{2}$ in. wide, each strip had approximately one-half of the strength of the 1-in. strip, or the same strength per unit cross-section. Reducing the width from 25.4 to 12.7 mm. had practically no effect upon strength per unit cross-section, but reducing the thickness from 1.0 to 0.5 mm. caused a very great loss in strength per unit cross-section. The effect of splitting becomes greater as the leather becomes thinner.

The resistance of the leather to stretch was found to vary directly with the strength. Measurements were made of the

load in kilograms required to stretch each strip to 1.25 times its initial length, and this value was called R , or the resistance to stretch. Splitting caused a percentage decrease in the value of R for both grain and flesh splits identical with the percentage decrease in strength. Thus Fig. 24 may be used to indicate the resistance of the leather to stretch simply by calling the ordinates "percentage of resistance to stretch of the unsplit leather."

Recovery after Stretching.—For some kinds of leather, such as belting, it is important to know to what extent the leather will tend to return to its original length after having been stretched. This is done by marking two points on the strip a given distance apart, applying a given load, noting the percentage stretch, and then removing the load and again measuring the distance between the two points. Balderston and Bowker (44) made a number of such tests on oak belting using strips 3.25 by 48 in. with points 36 in. apart. Under a stress of 1,000 lb. per square inch of cross-section, the leather increased 3.0 to 4.2 per cent in length. When the load was removed, the leather returned to from 1.002 to 1.007 times its original length, a recovery of from 93.3 to 83.3 per cent. Under a load of 2,500 lb. per square inch, the leather stretched from 9.7 to 10.8 per cent and, upon removal of the load, recovered from 83.3 to 82.5 per cent in length. One strip, upon standing for 48 hr., completely recovered its original length.

RESISTANCE TO TEARING

The authors determine resistance of upper leather to tearing with strips of leather 1 by 6 in. slit along the midline to the 3-in. mark. One of the slit ends is clamped in the upper jaw of the strength machine and the other in the lower. When the jaws are pulled apart, the leather is torn and the scale records the load required, which is taken as a measure of the resistance of the leather to tearing. Fleming used this to study the effect of splitting upon the tearing resistance of chrome retanned side upper leather 2 mm. thick. The unsplit leather required a load of 53 lb. or 24 kg. to tear it. Splitting caused a decrease in resistance to tearing practically identical with the percentage decreases in tensile strength shown in Fig. 24. The effect of splitting is evidently similar upon tensile strength, resistance to stretching, and resistance to tearing. A leather requiring 50 lb. to tear it is considered strong.

STITCH TEAR

In making shoe uppers, the leather is stitched, and it is sometimes desirable to know just how much it may be pulled without danger of the stitch pulling through the leather. Many methods have been devised to measure the so-called stitch tear. The one used by the authors is as follows (46): Cut circles of the leather with a die having a diameter of 3 cm. With a punch, cut a hole 3 mm. in diameter with its outer edge 2 mm. from the edge of the circle of leather. Clamp the leather in the upper jaws of the strength machine with the hole pointing downward. Through this hole pass a strand of Irish flax shoe thread (No. 6) and fasten to the lower clamp of the machine. Start the machine, allowing the lower clamp to pull the thread downward through the leather.

TABLE 19.—STRENGTH, STRETCH, AND STITCH TEAR OF 18 TYPICAL SHOE LEATHERS

Sample No.	Kind of leather	Average thickness, mm.	Kilograms required to break 2.54 cm. width	Tensile strength, kg. per sq. cm. cross-section	Per cent stretch at 100 kg. per sq. cm. cross-section	Stitch tear, kg.
1	Vegetable calf.....	1.19	128	422	9	13
2	Chrome calf.....	1.00	83	327	11	10
3	Glazed kid.....	0.76	79	409	23	8
4	Kangaroo.....	0.52	67	508	17	9
5	Cordovan.....	1.12	32	113	25	7
6	Buck.....	0.92	47	201	16	5
7	Chrome side.....	1.22	66	213	19	10
8	Suede.....	0.63	25	156	21	1
9	Calf lining.....	0.93	73	310	15	8
10	Sheep lining.....	0.87	44	200	18	6
11	Shark.....	0.80	24	118	38	5
12	Patent side.....	1.09	25	90	30	3
13	Patent kid.....	0.96	53	217	24	7
14	Patent colt.....	1.43	83	228	24	8
15	Heavy chrome.....	2.94	136	182	26	27
16	Chrome retan.....	2.48	218	346	17	28
17	Vegetable sole.....	6.28	305	191	11	38
18	Chrome sole.....	4.80	122	100	23	21

Table 19 gives values for stitch tear, strength and stretch for the 18 leathers whose analyses are given in Table 6, of

RESISTANCE OF GRAIN TO CRACKING

If very thick leather of low fat content is bent sharply with the grain side out, the grain surface will usually crack. In leathers, such as belting, it may be desirable to know how sharply the leather may be bent without danger of cracking the grain. Balderston (1) and Bowker (44) made such measurements on a sample of oak belting by placing a strip in a vise and bending it, grain side out, until the grain cracked and then measuring the radius of curvature at the point where the first cracking occurred. In a number of tests, the cracking occurred with values of radius of curvature from 1.6 to 3.2 mm.

Light leathers of high fat content rarely crack on bending sharply, but the grain may crack before the leather breaks in the measurement of tensile strength. In lasting a shoe, it may be important to know how much the leather may be stretched without danger of the grain cracking. This determination may be made at the same time as the tensile strength. While the leather is being stretched on the machine, the operator notes on the chart the point at which the grain cracks, which is easily seen. The chart then furnishes a record of the percentage of stretch at which the grain cracks and also a record of the stretch when the leather breaks. In many leathers, the two values coincide.

WEAR RESISTANCE

The only really satisfactory measurements of the relative resistance to wear of various leathers have been made by actual wearing tests. The two kinds of leather to be compared are made up into shoes, one kind going into the left shoe and the other into the right shoe for given tests. The shoes are widely distributed and periodic measurements are made of them. Since most of the wear occurs on the soles and heels, this method is used primarily in tests upon sole leather. Measurements are made of the time required to wear a hole through the sole or of the loss in weight or thickness of the sole in a given time.

Because this method is expensive and cumbersome, many attempts have been made to duplicate the results mechanically (2, 4, 6, 10, 15, 16, 25, 34, 59). Samples of sole leather are made

ANALYSIS OF LEATHER

to strike and scrape on a hard surface in a manner resembling the movement of the sole on the ground in walking. This method

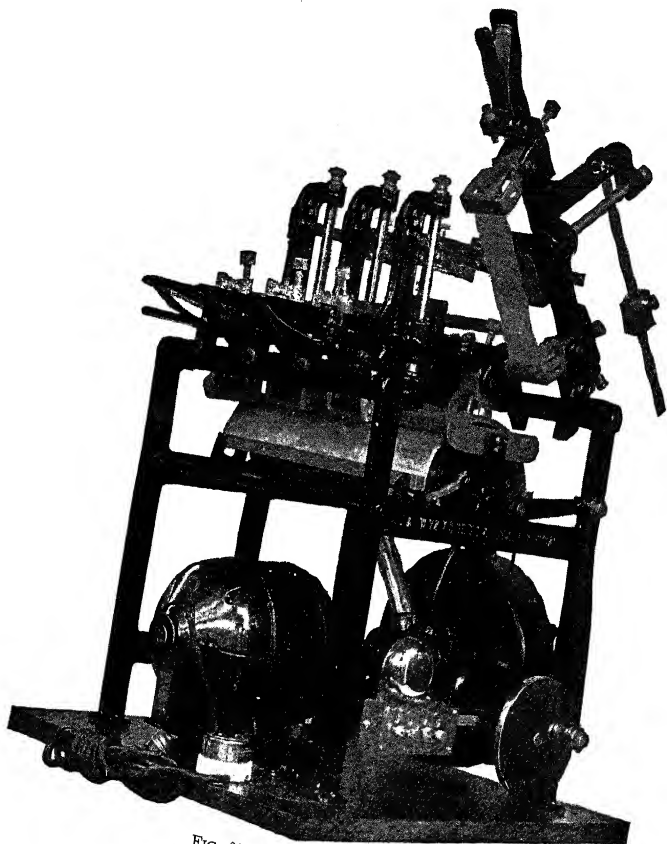


FIG. 25.—A precision test meter.

will show the resistance of the leather to abrasion but is not usually so satisfactory as the actual wearing tests for sole leather.

However, in the absence of actual wearing tests, mechanical measurements of the resistance of leather to abrasion may prove very valuable. For some leathers it may be that the only information desired is resistance to abrasion.

It will be sufficient to describe one machine designed for the purpose of measuring resistance to abrasion. In Fig. 25 is shown a machine known as a precision wear test meter. It has an oscillating semicircular drum, which is driven by a crank and connecting rod through a worm-gear speed reducer. A $\frac{1}{4}$ -hp. motor drives the machine at the rate of 90 double rubs per minute. This drum is equipped with full-length, toothed jaws, operated by a hand lever, which allows for conveniently placing and renewing the abrasive material on the drum. For testing leather, the abrasive material should be a No. 0 sandpaper, which can be renewed at regular intervals. In the rear of the machine is shown a large vacuum pump, which is piped to long narrow tubes, extending the full width over the drum. This serves to keep the abrasive surface free from dust of abrasion and also aids in maintaining a uniform temperature during the entire test.

The machine is made in two sizes, having either three or four overarms with sample holders. The picture shows the four-arm machine, in which four samples can be tested simultaneously under exactly the same conditions.

One of the overarms is raised to show how conveniently the sample can be placed in the rubber-covered clamps, and once it is placed in position, it need not be moved during the entire test, as the surface can be examined, or the thickness measured, without disturbing the original setting.

Each arm carries two graduated scale bars having sliding weights, by means of which the tension and the pressure of the sample can be adjusted to correspond to the wearing condition the material is to receive in actual practice. Adjustment is provided compensating for the thickness of the sample and for a possible stretching of the sample, allowing the scale bars always to be placed in the proper horizontal position. Thus the sample is squarely held to the abrasive surface under measured tension and pressure. The abrasive surface is kept cool, and the number of oscillations of the drum are registered on a counter. This counter is equipped with an alarm bell, which can be set to ring at a predetermined number. By taking a record of the readings of the machine, the conditions of the test can always be duplicated and accurate standards of quality developed.

A number of methods of utilizing the test may be suggested. It may be desirable to run a sample for a given number of rubs and then measure either the decrease in thickness or the decrease in weight. Or it may be preferred to determine the number of rubs required to produce a given decrease in thickness or in weight. For some kinds of leather, it may be desirable to note the effect of a given number of rubs upon the tensile strength and stretch of the leather; or to measure the number of rubs required to produce a given loss in tensile strength or in resistance to stretching.

The machine may be used also to measure the effect of finishing materials upon resistance to abrasion. In some cases, it may be desirable to note the number of rubs required to remove the finishing material as observed visually.

VENTILATING PROPERTIES

The animal body gets rid of its excess heat through the evaporation of the water of perspiration from the surface of the skin. If the foot is so confined that the perspiration at its outer surface cannot diffuse away or evaporate, it will become hot and uncomfortable. The perspiration inside the shoe tends to maintain a relative humidity of 100 per cent in the confined atmosphere. In order to prevent discomfort, the leather of the shoe must remove the water from this inner, humid atmosphere and pass it on to the outer atmosphere of lower relative humidity. Good shoe-upper leather has the power to do this very effectively. This property has been referred to as "permeability to water vapor."

Permeability to Water Vapor.—The essential part of the apparatus used to measure the power of leather to conduct water from an atmosphere of high to one of low relative humidity is shown in Fig. 26 (56). It consists of a wide-mouth bottle having a capacity of 70 cc. and fitted with a screw cap, in which a hole 1.4 cm. in diameter has been cut. The leather sample is cut with a circular die having the same diameter as the two brass disks used—namely, 3.0 cm. In the center of each disk a hole is cut exactly 1.27 cm. in diameter which allows an area of exactly 1.267 square centimeter of leather to be exposed. The leather is placed between these two brass disks and set in the cap as shown. A tightly fitting cork having a hole in its center 1.4 cm.

in diameter is then inserted. The cork resting on the rim of the bottle effects a water-tight seal.

Exactly 25 cc. of pure sulfuric acid is put into the bottle, and then bottle and acid, without the cap, are weighed. The cap containing the leather is then screwed into place and the whole is placed into an ordinary individual desiccator containing water, and this in turn is submerged in a large thermostat constant to $0.1^{\circ}\text{C}.$ ¹ The acid inside the bottle tends to maintain an atmosphere of practically 0 relative humidity, while the water in the desiccator tends to maintain an atmosphere of 100 per cent relative humidity. The only way that water can pass from the outer humid atmosphere to the inner dry one is through the leather. In order to determine how much water has passed through the 1.267 sq. cm. of leather area in unit time, it is only necessary to remove the bottle and weigh it with the cap removed. The object in removing the cap before weighing each time is to avoid fluctuations due to the changing water content of the leather and cork.

Effect of Temperature.—In using this method, Wilson and Lines (56) first determined the effect of temperature and relative humidity. In studying the effect of temperature, two series of these pieces of apparatus were set up. In one series the caps contained disks of vegetable-tanned calf leather all taken from the butt of the same skin. In the other series no leather was used, but the holes in the disks allowed free contact of the wet and dry atmospheres over the area of 1.267 sq. cm. In the leather series, all grain surfaces were exposed to the dry and the flesh surfaces to the wet atmosphere, as would be the case in the wearing of a shoe. The desiccators were placed in thermostats at different temperatures and the bottles were weighed once each day for a week. The gain in weight per day varied only very slightly throughout the week. The results are shown in Fig. 27

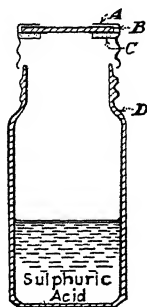


FIG. 26.—Apparatus to measure the rate of passage of through leather from an atmosphere of high to one of low

minum screw cap with hole 1.4 cm. in diameter. B. Disk of leather sandwiched between two brass disks each with a hole exactly 1.27 cm. in diameter. C. Tightly fitting cork with hole 1.4 cm. in diameter. D. Bottle of 70 cc. capacity.

¹ If a blank without leather is run with each set of determinations, the thermostat is unnecessary. See working directions below.

and Table 20. Bradley, McKay, and Worswick (7) have shown that the rate of gain in weight with time varies with the length of the air column in the bottle. Their results show the necessity for having all dimensions and quantities rigidly the same in all comparative tests.

Two factors are worthy of special note. The first is the large amount of water passed by the leather as compared with that passing through free space; the leather in service actually exhibited water-repelling properties in shedding rain. The second is the practical constancy of the ratio of the amount of

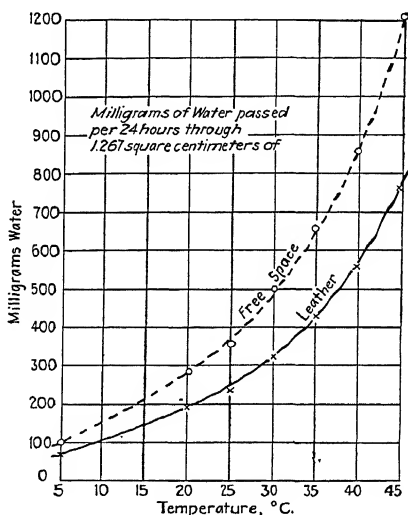


FIG. 27.—Effect of temperature upon the passage of water from an atmosphere of 100 per cent relative humidity to one of 0 relative humidity through vegetable-tanned calf leather and through free space.

water passed by the leather to that passed through free space over the entire range of temperature, as shown in Table 20. Over the range 20 to 40°C., there is a deviation of only one unit from 66 per cent, which is quite within the limits of experimental error.

Effect of Relative Humidity.—Wilson and Lines (56) then studied the effect of varying the relative humidity of the atmosphere inside the bottles. Six solutions were made up containing the following concentrations of sulfuric acid in moles per liter:

TABLE 20.—EFFECT OF TEMPERATURE UPON PASSAGE OF WATER FROM ATMOSPHERE OF 100 PER CENT RELATIVE HUMIDITY TO ONE OF ZERO RELATIVE HUMIDITY ACROSS AN AREA OF 1.267 SQ. CM., THROUGH FREE SPACE AND THROUGH LEATHER

Temperature, degree centigrade	Milligram water passed per 24 hr. through		Ratio, per cent
	Leather	Free space	
5	71	98	72
20	192	286	67
25	236	360	66
30	328	505	65
35	430	660	65
40	560	863	65
45	765	1,214	63
			Average 66

18.7, 8.8, 6.8, 5.1, 3.3, and 0.0. These, when placed in the bottles, tend to give the atmospheres above them relative humidities of 0, 20, 40, 60, 80, and 100 per cent, respectively (57). Disks cut from the same piece of leather as that used in the temperature experiment were employed and the desiccators were all kept in a thermostat at 25°C. The results are shown in Fig. 28 and Table 21.

TABLE 21.—EFFECT OF RELATIVE HUMIDITY OF ONE ATMOSPHERE UPON PASSAGE OF WATER INTO IT FROM ATMOSPHERE KEPT AT 100 PER CENT RELATIVE HUMIDITY ACROSS AN AREA OF 1.267 SQ. CM. THROUGH FREE SPACE AND THROUGH LEATHER AT 25°C.

Per cent relative humidity	Milligram water passed per 24 hr. through		Ratio, per cent
	Leather	Free space	
0	236	360	66
20	179	282	63
40	143	217	66
60	91	134	68
80	51	78	65
100	0	0	
			Average 66

The rate of passage of water in both series appears to be a straight-line function of the difference in relative humidity between the two atmospheres, and the ratio of the rate of passage through this leather to the rate of passage through free space appears to be constant at 66 per cent at all relative humidities. Since this ratio appears to be independent of temperature and of difference in relative humidity, it can be used as a constant characteristic of any given sample of leather and is taken as the measure of the permeability of that leather to water vapor.

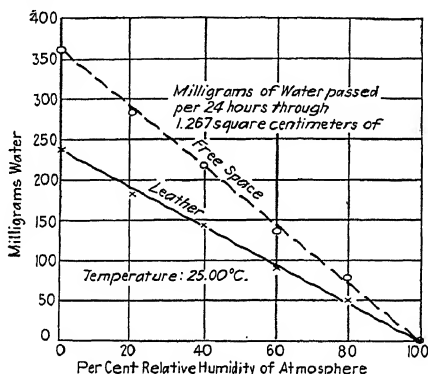


FIG. 28.—Effect of relative humidity of one atmosphere upon passage of water into it from an atmosphere of 100 per cent relative humidity through vegetable-tanned calf leather and through free space.

Making the Determination.—Cut two disks of leather from the butt of each skins to be tested, using a sharp die having an area of 3.0 sq. cm. Insert the disks in the covers of two bottles like those shown in Fig. 26 with the grain side down, *i.e.*, toward the acid. Measure with a pipette exactly 25 cc. of concentrated sulfuric acid into each of the two bottles, and also into two additional bottles to serve as blanks. Weigh the bottles with their acid charges but without their covers, to the nearest 5 mg. Screw on the covers, using covers without leather disks for the two blanks, and set each bottle in an ordinary desiccator containing water so that the bottle is about half submerged. Let stand at room temperature for 24 hr. Remove each bottle from the water, wipe dry with a clean towel, and reweigh. The average gain in weight of the two bottles with the leather disks is the amount of water passed through the leather, and the average gain in weight of the two blanks is the amount of water passed through free space. The ratio of these two averages is the ventilating power of the leather.

$$\text{Ventilating power} = \frac{\text{av. g. H}_2\text{O passed through leather} \times 100}{\text{av. g. H}_2\text{O passed through free space}}$$

Relative Porosity.—In order to determine whether any relation might exist between the permeability factor and the degree of porosity of the leather, Wilson and Lines (56) made measurements of the latter with the apparatus pictured in Fig. 29. The disk of leather used in the permeability measurement was transferred, in each test, to the slot of the brass receptacle *B*. *D* was then screwed tightly into *B* so that no air could pass through the system without passing through the leather. The vacuum pump was then run so as to maintain a constant reading of 63.5 cm. (25 in.) on the vacuum gage. The amount of air passing through the leather was measured by the volume of water passing from

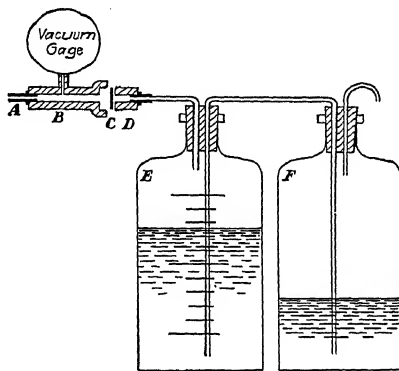


FIG. 29.—Apparatus for measuring the porosity of leather. *A*. Outlet to vacuum pump and chambers. *B*. Brass receptacle for holding leather, with hole 1.27 cm. in diameter and outer well 3 cm. in diameter. *C*. Leather disk 3 cm. in diameter. *D*. Brass plug with screw to fit into *B* and with hole 1.27 cm. in diameter. *E*. Calibrated bottle containing water to measure rate of passage of air through leather disk.

bottle *F* to bottle *E*, which could be read directly from the calibration marks on bottle *E*. Measurements were recorded in terms of relative porosity, defined as the number of cubic centimeters of air passed through 1 sq. cm. of leather per minute when the gage reading is kept constant at 63.5 cm.

Effect of Finishing Materials.—Wilson and Lines (56) treated disks of vegetable-tanned calf leather with successive coatings of finishing material, between each of which they were dried and polished with wool. The amount of dry material used in each coating was measured by the weight of the coat applied, determined by noting the loss in weight of the bottle containing the finish. In one series, an aqueous solution of casein was used

and in the other a solution of collodion in a mixture of alcohol and ether.

The effect of casein is shown in Fig. 30 and of collodion in Fig. 31. It is apparent that any relation between porosity and

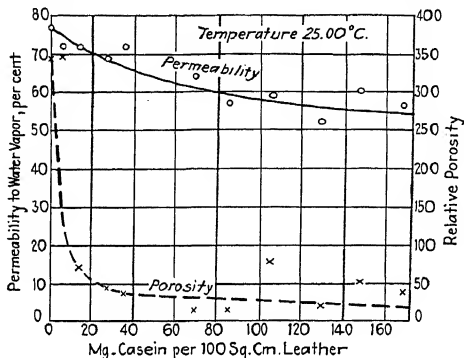


FIG. 30.—Effect of casein finish upon ventilating properties of vegetable-tanned calf leather.

permeability to water vapor cannot be more than an indirect one. In the casein series, samples 2 and 5 have the same permeability but differ enormously in relative porosity.

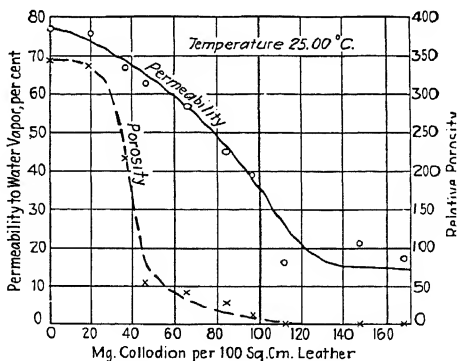


FIG. 31.—Effect of collodion finish upon the ventilating properties of vegetable-tanned calf leather.

The effect of the oil content of leather is shown in Fig. 32. A series of disks of vegetable-tanned calf leather was completely degreased with chloroform and then soaked in chloroform solu-

tions of neat's-foot oil of different strengths. The disks were then freed from chloroform and used in the tests, after which the oil contents were determined. Increased oil content brings about a decreasing permeability and porosity, but again we note no definite relation between the two.

Varo, working in the authors' laboratories, made a very extensive study of the effects of various finishes and methods of finishing upon the permeability of leather to water vapor and upon its relative porosity. He studied first the effect of glazing colored chrome calf leather to which no finishing material had been applied. The initial permeability value was 88. The first glazing reduced it to 80, the second to 78, and the third to 76.

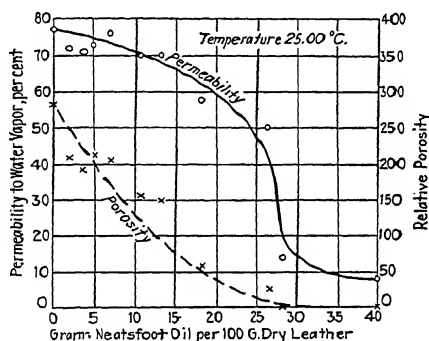


FIG. 32.—Effect of oil content of leather upon its ventilating properties.

Subsequent graining or boarding did not change this value. The relative porosity was initially 600. The first glazing reduced it to 300, the second to 180, and the third to 170. Subsequent graining brought it back to 250. This work was repeated with the application of a great variety of finishing materials preceding each glazing.

Shellac preparations caused a greater decrease in ventilating properties than protein finishes. Pressure-treated gelatin, gum arabic, soluble starch, and linseed extracts increased the ventilating power over that of leather glazed without finishing. Waxes, sulfonated oils, pigments, dyes, and varnishes all decreased the ventilating properties. The great decrease in ventilating properties caused by lacquers and varnishes in making patent leather was shown to be due primarily to the large quantities

applied; when applied in quantities comparable with the amounts of shellac, casein, and other finishing materials ordinarily used on leathers, they caused no greater decrease in ventilating power. The graining or boarding of leathers after finishing and glazing causes an increase in ventilating power, probably because this operation produces tiny breaks in the hardened film of finishing material.

Other Methods.—Many methods have been devised for measuring the permeability of leather to liquid water (3, 11, 12, 19, 20, 23, 28, 33, 36). Among the more recent is one by Orthmann (24) in which the test is made by cutting a piece from a bend of sole leather and making sandals from it in such manner as not to pierce the leather completely. The sandals are worn by a man who walks in a shallow pool of water on a concrete floor, 120 steps to the minute, and notes the time in minutes required for water to penetrate to the ball of the foot. A value of 30 min. was obtained for the retan sole leather, the thickness of which in a sandal was 4.1 mm.

Bergmann (3) devised instruments for measuring both the permeability of leather and that of raw skin to water and to gases under pressure. The permeability to water for skin or leather was always greater from the flesh side to grain side than in the other direction. When leather was split, the grain split was more permeable than the flesh split. Bergmann and Ludewig (3) found that the permeability of leather to gas under pressure decreased with increasing water content of the leather.

WATER ABSORPTION

Whitmore and Downing (39) use a method in which blocks of leather are soaked in water and the increase in weight measured after 2 and after 24 hr. At the end of 24 hr., the leather is considered to be saturated with water unless it is a waterproof leather. The ratio of amount of water absorbed in 2 hr. to that absorbed in 24 hr. is called the percentage saturation for 2 hr. The ratio was found to vary from 55 to 100 per cent for blocks of vegetable-tanned sole leather tested.

The method employed by the authors is as follows: Cut a disk of the leather with a circular die of 3 cm. diameter and weigh. Soak in 25 cc. water at 70°F. in tared, covered dish for 30 min. Withdraw disk with forceps, shaking adhering water back into dish. Do not blot the piece. Evaporate watery solution to dryness and weigh residue. Put disk into a

second dish with 25 cc. of water at 70°F. and let stand 23.5 hr. Remove and weigh again. Evaporate watery extract and weigh dry residue.

Add weight of first residue to total weight of leather after 30 min. Subtract initial weight of disk. Multiply by 100 and divide by initial weight to get percentage of water absorbed in 30 min. Add weights of both residues to that of disk after 24 hr. in water. Subtract initial weight. Multiply by 100 and divide by initial weight to get percentage of water absorbed in 24 hr.

DIMENSIONAL CHANGES WITH RELATIVE HUMIDITY (48, 53)

Method.—Cut a sample of leather about 55 cm. long and about 10 cm. wide. Suspend it above a 10.2-normal solution of sulfuric acid in a desiccator and leave it there for 3 days. Then cut it into six strips each 50 cm. long and 1 cm. wide. Weigh the strips and measure their average thicknesses, making a water determination on the remainder of the sample.

In the bottoms of six desiccators place sulfuric acid solutions of the following normalities: 37.5 (concentrated), 17.6, 13.6, 10.2, 6.6, and 0, which tend to maintain relative humidities in the atmospheres above them of 0, 20, 40, 60, 80, and 100 per cent, respectively. Place a cross of copper wire above the acid solution in each desiccator, coil the strip of leather and allow it to rest upon the cross so as not to have any direct contact with the acid. Small desiccators should be used and only one strip of leather placed in each. The desiccators may be kept at any desired constant temperature, and the rate of change of area measured at any given intervals of time. In making a measurement the strip should be removed from the desiccator, its length, weight, and average thickness measured accurately, and the strip returned to the desiccator in a space of less than 2 min. Since equilibrium is attained only after many weeks, it may be sufficient to set some definite period of time which shall be the same for all samples tested. For shoe-upper leathers the measured length should be squared so as to show the relative change in area. When leather increases in volume, the thickness usually increases at a much greater rate than either of the other two dimensions. From the water content of the original sample and the changing weights one can calculate the changes in water content. The preliminary keeping of the large sample in a desiccator with an atmosphere of 60 per cent relative humidity is to insure uniformity of water content of the entire sample. Care must always be exercised not to permit any sample of leather to remain out of the atmosphere of constant relative humidity any longer than is absolutely necessary. When plotting curves showing the change in dimensions or in weight with relative humidity it is customary to take the values at 0 relative humidity as unity.

Typical Examples.—Figure 33 shows the effect of relative humidity upon the water content of chrome and vegetable-tanned calf leathers, as found by Wilson and Gallun (48). Figure 34 shows the increasing changes in area.

Wilson and Kern (53) measured the increase in area and water content with increasing relative humidity of the atmosphere of

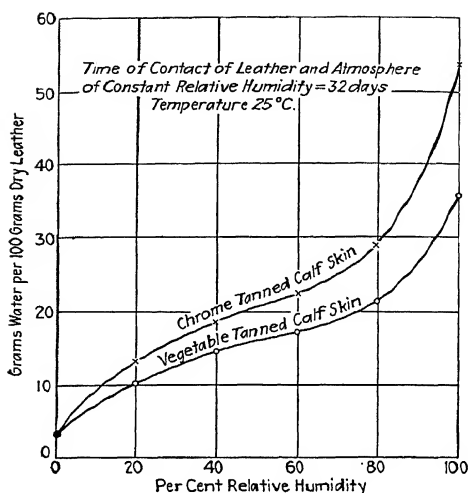


FIG. 33.—Showing effect of the relative humidity of the air upon the water content of chrome and vegetable-tanned calf leathers.

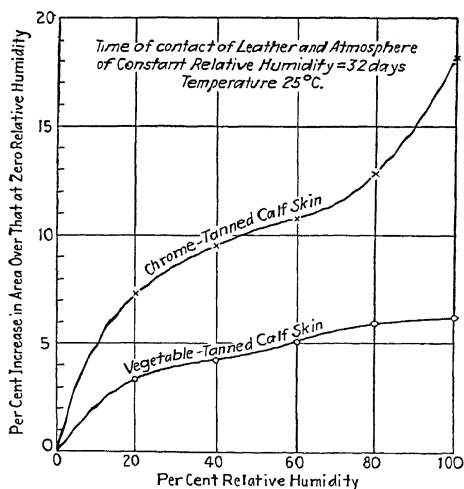


FIG. 34.—Showing how the area of chrome and vegetable-tanned calf leathers varies with the relative humidity of the atmosphere.

the 18 typical shoe leathers whose analyses are given in Chap. II. The temperature of the experiments was 25°C. Table 22 shows the water content after 30 days' contact with atmosphere of different relative humidities. Table 23 shows the area change with increasing relative humidity. Table 24 shows the changing areas with time. In studying these figures, it should be noted, in the ratio of the area at 100 per cent relative humidity to the area at 0 relative humidity, that both numerator and denominator

22.—WATER CONTENTS OF VARIOUS LEATHERS AFTER 30 DAYS' CONTACT WITH ATMOSPHERES OF DIFFERENT RELATIVE HUMIDITIES

Sample No.	Kind of leather	Grams water per 100 g. dry leather after 30 days at relative humidity of						
		20%	40%	50%	60%	80%	100%	
1	Vegetable calf.	1.4	10.8	14.0	15.7	17.9	21.2	39.6
2	Chrome calf.	2.1	12.4	18.1	19.5	21.0	27.9	53.4
3	Glazed kid.	2.9	10.6	14.2	15.9	18.1	27.3	62.2
4	Kangaroo.	0.4	9.3	12.6	13.6	15.4	22.8	51.7
5	Cordovan.	1.8	7.0	9.8	11.1	11.8	15.6	22.9
6	Buck.	2.2	11.7	15.4	16.4	17.4	25.1	47.8
7	Chrome side.	1.8	12.1	17.2	19.5	20.8	25.9	54.5
8	Suede.	0.3	9.4	13.4	14.5	15.8	20.9	59.5
9	Calf lining.	0.9	8.8	12.1	13.5	16.1	19.6	32.0
10	Sheep lining.	1.1	8.2	11.3	12.2	14.6	19.6	48.4
11	Shark.	2.4	10.2	12.7	13.9	14.3	17.1	38.1
12	Patent side.	0.7	8.5	10.4	11.2	12.6	18.5	36.9
13	Patent kid.	1.9	10.5	12.7	13.4	14.6	20.7	39.5
14	Patent colt.	2.0	9.6	12.4	13.6	15.1	22.7	57.5
15	Heavy chrome	1.2	12.9	15.1	16.8	17.7	21.9	49.6
16	Chrome retan.	4.4	12.5	16.4	17.8	18.4	21.1	37.8
17	Vegetable sole.	3.4	12.2	17.0	17.1	18.3	21.7	43.6
18	Chrome sole.	8.6	14.9	18.1	19.5	20.6	24.5	50.4

are changing with time. If the test had been carried out with the leathers initially in equilibrium with a dry atmosphere, the change the first day would have been much greater.

An example of this is shown in Fig. 35 for a light chrome calf leather and a heavy chrome side leather, not included in the 18 leathers being studied. After 14 days the two leathers were returned to the dry atmosphere, and the curves illustrate the reversibility of the process. In going from one extreme of relative humidity to the other, the change is very rapid; the chrome calf

leather increased more than 11 per cent in 4 hr. and showed a correspondingly large decrease in area when first returned from the wet to the dry atmosphere. Thickness may explain the difference in rate of change between these two leathers, but it will not explain why the vegetable-tanned sole leather reached equilibrium in much less time than the very thin kangaroo leather.

TABLE 23.—AREA CHANGE OF VARIOUS LEATHERS WITH INCREASING RELATIVE HUMIDITY OF THE ATMOSPHERES

Sample no.	Kind of leather	Per cent increase in area with increasing relative humidity above zero at relative humidity					
		20 %	40 %	50 %	60 %	80 %	100 %
1	Vegetable calf.	3.6	4.2	4.5	4.8	5.5	5.7
2	Chrome calf...	7.7	10.0	10.3	11.5	12.4	16.0
3	Glazed kid....	3.4	4.6	4.8	5.5	7.5	15.6
4	Kangaroo.....	5.7	6.9	6.9	7.5	10.9	19.0
5	Cordovan.....	2.0	3.0	3.0	3.2	3.4	4.0
6	Buck.....	6.7	7.5	7.7	8.8	10.5	14.7
7	Chrome side...	6.7	7.7	8.0	9.2	10.5	15.8
8	Suede.....	8.0	10.7	10.9	11.7	11.9	13.8
9	Calf lining....	5.3	6.5	6.7	6.9	7.5	9.2
10	Sheep lining...	4.2	5.5	5.5	5.9	8.2	9.4
11	Shark.....	4.0	4.9	5.1	5.3	5.7	8.0
12	Patent side....	5.5	6.3	6.3	6.9	8.6	10.5
13	Patent kid....	5.3	5.9	6.1	6.5	7.1	9.6
14	Patent colt....	4.5	6.3	6.3	6.5	8.2	13.0
15	Heavy chrome	7.1	8.0	8.0	9.2	10.9	16.9
16	Chrome retan.	6.5	7.7	8.0	8.4	9.0	11.5
17	Vegetable sole.	1.0	1.4	2.7	3.0	3.0	5.5
18	Chrome sole...	3.8	4.5	5.9	6.3	7.7	13.0

No single factor will explain all of the differences in area change found for the different leathers. At the 100-day period, the extreme area change for the vegetable-tanned leathers varied from 4.0 to 9.6 per cent, with an average of 7.1 per cent; and for the chrome leathers from 10.7 to 19.5 per cent, with an average of 15.2 per cent. The effect of kind of tannage is clearly very great and the one outstanding cause for big differences. The lacquered surfaces may explain why the area changes for the patent leathers are lower than for the other chrome leathers.

One might be tempted to suggest that the extremely low area change of the cordovan leather was due to its high fat content, were it not for the fact that the kangaroo leather also has a high fat content and yet shows the greatest area change of all. Of course it is possible that the kangaroo leather might have shown a still greater area change had its fat content been lower; several samples of chrome calf leather were examined showing area changes greater than 23 per cent.

TABLE 24.—PERCENTAGE BY WHICH AREA AT 100 PER CENT RELATIVE HUMIDITY EXCEEDS THAT AT ZERO RELATIVE HUMIDITY AFTER DIFFERENT PERIODS OF TIME SINCE LEATHER WAS TRANSFERRED FROM AN ATMOSPHERE OF 50 PER CENT RELATIVE HUMIDITY TO ATMOSPHERES OF 0 AND 100 PER CENT RELATIVE HUMIDITY, RESPECTIVELY

Sample No.	Kind of leather	1 day	2 days	6 days	13 days	20 days	30 days	100 days
1	Vegetable calf..	2.0	3.2	4.4	4.9	5.5	5.7	5.7
2	Chrome calf...	10.4	11.5	13.4	15.8	16.0	16.0	16.4
3	Glazed kid....	8.8	9.6	12.8	14.9	15.6	15.6	15.6
4	Kangaroo.....	8.6	9.8	13.4	16.6	17.3	19.0	19.5
5	Cordovan.....	2.4	3.0	3.8	4.0	4.0	4.0	4.0
6	Buck.....	8.0	9.0	10.3	14.5	14.7	14.7	14.9
7	Chrome side...	7.5	8.6	12.8	15.1	15.3	15.8	16.9
8	Suede.....	7.5	8.0	10.7	13.0	13.8	13.8	14.1
9	Calf lining.....	5.9	6.9	7.7	9.0	9.2	9.2	9.4
10	Sheep lining...	6.5	7.5	9.0	9.4	9.4	9.4	9.6
11	Shark.....	3.8	4.4	5.5	7.5	7.9	8.0	8.2
12	Patent side....	5.7	7.1	9.0	9.8	10.0	10.5	11.1
13	Patent kid.....	4.9	6.1	8.2	9.0	9.4	9.6	10.7
14	Patent colt....	7.5	8.8	11.3	12.8	12.8	13.0	13.6
15	Heavy chrome..	5.5	8.4	12.8	15.6	16.4	16.9	18.8
16	Chrome retan...	4.4	5.7	9.2	10.7	11.1	11.5	12.4
17	Vegetable sole.	3.4	3.7	4.4	4.9	5.5	5.5	5.5
18	Chrome sole...	4.4	6.0	9.0	11.3	12.4	13.0	15.3

Practical Tests.—Wilson and Gallun (48) made a number of practical tests under rigidly controlled conditions. Several calfskins were cut into sides, and one of each was chrome tanned and the other vegetable tanned. For each man taking part in the test, two pairs of shoes were made, one pair from the chrome-tanned and the other from the vegetable-tanned side of the same skin. During one period, he would wear a chrome-leather shoe

on the left foot and a shoe of vegetable-tanned leather on the right foot and then reverse this during another period. When the weather was damp, the chrome shoe was too big, and when the weather was very dry, it was too tight to be comfortable. This was noticeable to a very much lesser degree with the shoes of the vegetable-tanned leather. After entering a warm, very dry room when it was cold outside, the difference in shrinking and tightening of the two shoes was very marked.

In one test, a shoe of each kind was kept for several days in an atmosphere of 100 per cent relative humidity and then transferred to one of 0 relative humidity. The width of the upper of the chrome shoe, measured just back of the toe cap, was found

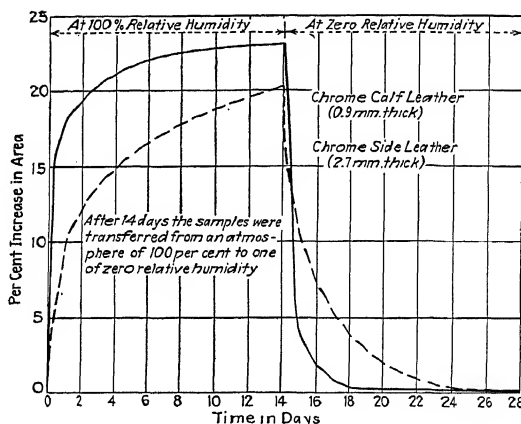


FIG. 35.—Area change of leather with time following a sudden change in the relative humidity of the atmosphere from 0 to 100 per cent and then back again to 0.

equal to a standard D width at 100 per cent relative humidity but decreased to the equivalent of a B width when kept for a week at 0 relative humidity. The change in the shoe of vegetable-tanned leather was only about one-third as great. In some cases, the man making the test could not squeeze his foot into the chrome shoe when it had just been taken from an atmosphere of 0 relative humidity.

A glance at Figs. 32 and 33 will show that the curves are flattest in the region of 50 per cent relative humidity. Where there is not great variation in relative humidity from this value,

one would not expect to find much difference in the size changes between shoes made of the two kinds of leather. The greater shrinkage of the chrome leather is somewhat offset, also, by its greater ease of stretch. But where the conditions are severe, the kind of tannage becomes an important factor in foot comfort. Greeves (14) quotes an officer of long experience in the World War, and one who knew a great deal about leather, to the effect that chrome shoes were most uncomfortable to sleep in, many soldiers risking trench feet and frostbite rather than lying down in chrome shoes. It is also reported that there was always a rush on the part of soldiers who knew the difference in comfort to get vegetable-tanned shoes. Sportsmen who have made the test say that at the end of a day's tramping for shooting, the feet ache less in vegetable-tanned than in chrome shoes. The work of Wilson and Gallun received very wide newspaper publicity throughout the world as having solved the riddle of the weather prophet who foretells changes in the weather by the pain in his corns. The corns merely respond to shrinkages in the leather of the shoes.

Theoretical Considerations.—The dimensional changes in leather with relative humidity will undoubtedly receive much attention in the future; it has received surprisingly little in the past. The cause of the much greater changes in chrome leather than in vegetable-tanned leather is still a matter for speculation. Collagen has a great affinity for water, and chrome leather, on an average, contains much more collagen per unit volume than vegetable-tanned leather. Analyses of more than 50 chrome calfskins showed an average of 0.44 g. of collagen per cubic centimeter of leather against 0.32 g. of collagen for a similar number of vegetable-tanned calfskins. It may be that vegetable tannins combine with chemical groups of the collagen molecule that would otherwise take up water to a greater extent than do chromium nuclei in chrome tanning. On the other hand, the greater tendency for chrome leather to take up water may be due to the affinity of the chromium nucleus for water. The vegetable retanning of chrome leather brings about a great reduction in affinity of the leather for water. It is possible that even the relatively small dimensional changes of vegetable-tanned leather can be further reduced by some appropriate treatment. Much of the future foot comfort of the human race may depend upon an exhaustive study of these considerations.

RESISTANCE TO HEAT (8)

A test commonly made to determine the degree of tannage of leather is to measure its resistance to heat when wet. To make the test cut a strip of leather 10 by 1 cm. and suspend in a beaker. Raise the temperature of the water gradually and record the temperature at which the leather begins to curl or shrink. This is known as the shrinking temperature. An oil-tanned leather will usually shrink at temperatures under 60°C., whereas a heavily chrome-tanned leather will not shrink in water at the boiling point.

RESISTANCE TO ACIDS

Different leathers may show very great differences in their resistance to the action of mineral acids which may be measured in two ways: Either the leather may be placed in a series of sulfuric acid solutions of different strengths, or it may be treated with different amounts of acid to give a wide range of acid contents as shown by analysis. In either case, the test is made by noting the loss in tensile strength with time.

In selecting samples for the test, it must be remembered that the tensile strength of a skin varies greatly over its area, as shown in Fig. 20. The method developed by Wilson (43) is illustrated for a concrete case in Fig. 23. A piece of finished chrome calf leather 75 by 17 cm. was cut into 25 strips each 3 by 17 cm. numbering from 1 to 25. The odd-numbered ones were measured for tensile strength exactly as directed earlier in this chapter. The even-numbered ones were wet with solutions of different hydrogen-ion concentration, ranging from half-normal sodium bicarbonate to five-normal sulfuric acid. The sodium bicarbonate solutions were used to get strips of leather containing less than the usual amount of sulfuric acid. The strips were blotted, air-dried and kept for 6 months to age. Then their tensile strengths were measured and plotted along with those for the untreated strips in Fig. 23. The broken strip in each test was analyzed for water and sulfuric acid; the latter value is recorded on the graph.

Up to an acid content of about 10 per cent the two curves practically coincide, but they diverge sharply with further increase in acid content, the acid-treated strips finally losing all measurable strength. The distance between the two curves gives a measure of the progressive loss of strength with increasing

percentage of acid in the leather. For example, take strip No. 16 with a tensile strength of 79. A line drawn directly upward to the upper curve intersects it at the value 168, which may be taken as the strength of No. 16 before the acid treatment and ageing. We may therefore conclude that the treatment has caused the leather to suffer a loss of 53 per cent in strength. This procedure enables one to determine the percentage loss in strength of leather resulting from any special treatment. In each test, the acid content of the leather was determined in the strip used for measuring the tensile strength.

In this experiment the time was set at 6 months. The effect of ageing for longer periods of time was determined by repetitions of the experiment with longer time intervals.

TEMPERATURE RISE IN SUNLIGHT

Wilson and Diener (47) made a study to determine how much the color of the leather has to do with the heat developed when a shoe is exposed to sunlight. On a clear summer's day, if one keeps one's foot in the sunlight very long, it will get uncomfortably hot. If, now, a black shoe is put on one foot and a light-colored one on the other, a big difference in temperature will be felt, the foot housed in the black shoe feeling much the hotter.

Certain materials appear black only because they do not reflect light but convert it into heat. White light contains all colors, and the lighter in shade any material is the more colors of white light it reflects and the less it converts into heat. Few people seem to appreciate how great is the difference in temperature rise between black and light-colored leathers when placed in direct sunlight. Wilson and Diener measured the difference for eight samples of vegetable-tanned calf leathers. In each test, the bulb of a standard laboratory thermometer was covered with a single thickness of leather, and all were put in the sunlight at the same time. In only a few minutes the temperature rose to values considerably higher than the air temperature of 60°F., but to a different degree for each color of leather. The values given in Table 25 are typical of the results.

The black leather actually registered 16° warmer than the light straw-colored leather in direct sunlight. The temperatures were reached in a few moments and did not go any higher. In repeated tests, the actual values obtained varied, but the relative order was maintained. The amount of mist in the air, velocity of

TABLE 25.—TEMPERATURE OF LEATHERS OF DIFFERENT COLOR IN SUNLIGHT

Color of leather	Temperature in sunlight, degrees Fahrenheit
Light straw.....	100
Sandy.....	102
Very light tan.....	105
Light tan.....	106
Medium tan.....	107
Dark tan.....	110
Very dark tan.....	111
Black.....	116

wind, moisture in the leather, and kind of tannage affect only the absolute values; the relative values depend upon color. Values obtained with chrome leather were essentially the same as those obtained with vegetable-tanned leathers. The results show the advantage of wearing light-colored shoes during the day in summer and black shoes in winter.

TEMPER

One of the methods used by the shoe manufacturer to judge the quality of leather for shoe uppers is to fold the right side of the skin over the left, flesh side in, and then run his hand up and down the region of the backbone, noting the pressure required to squeeze the two sides together and the vigor of rebound of the leather upon release of the pressure. The property measured in this crude way is generally known as temper, and it is recognized that temper has an influence upon both the comfort of the shoe and its appearance in actual wear.

Wilson (45) has studied the property called temper and devised a method for the quantitative measurement of its two components, flexibility and recovery. The apparatus is pictured in Fig. 36. The base is a solid maple block into which an iron rod is set vertically. From an adjustable arm attached to this rod, a balance pan with flat base is suspended by means of a spiral spring of appropriate size. Attached to another adjustable arm is a scale 4 cm. long with 100 equal divisions. A fine wire to be used in reading the scale is drawn across the pan supports. The position of the scale is set to give a reading of zero when the pan rests upon the block.

The leather to be tested is cut with a die 1 by 6 in. Tack holes are punched near the ends of the leather 12.57 cm. apart and

equidistant from the sides. The leather is drawn into a circle, grain side out, and the ends are joined by means of a thumb tack, which is inserted in the block at a point corresponding to the vertical projection of the center of the pan on the block. If the leather has a negligible thickness and forms a perfect circle, when weights enough are placed on the pan to bring it to the point where it just touches the leather, the scale reading will be 100, since the diameter of a circle with circumference of 12.57 cm. is 4 cm., which is the length of the scale. Unfortunately, the finite and variable thickness of leather strips to be tested complicates the measurement and necessitates the establishment of arbitrary standards.

Effect of Pressure.—Figure 37 shows how the scale reading varied for a strip of chrome calf leather, 0.90 mm. thick, when an increasing load was placed upon the pan. The curve resembles the familiar die-away curve of the hyperbolic type. After the diameter of the circle of leather has been reduced to less than one-quarter of its initial value, it ceases to be sensitive to small increases in pressure. Further compression tends to crease the leather in two places, pulling apart the fibers in the grain layer and crushing together those in the flesh layer. The resistance of the leather to this further compression involves more than is included in the term *temper*. The reading at which this extra resistance becomes apparent increases with the thickness of the strip of leather being tested.

Arbitrary Standards.—In comparing temper values of different leathers, it seemed logical to select some degree of compression that would correspond to the qualitative test made by the shoe manufacturer, that would be great enough to test the ability of the leather to recover, that would be small enough to avoid too

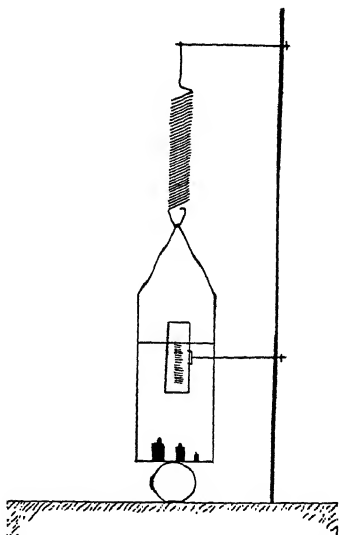


Fig. 36.—Apparatus for measuring the temper of leather.

great complication due to including the extra resistance not involved in temper, and that would compensate for variations in thickness of different leathers.

If the scale reading when the pan just rests upon the circle of leather is 100, the pan can be forced down to a point a distance above the block equal to two thicknesses of leather. One millimeter equals 2.5 units on the scale. Taking t as the thickness of the leather in millimeters, the pan may be forced through a distance equal to $100 - 5t$ units on the scale. In his work, Wilson selected the arbitrary value for degree of compression equal to three-quarters of this, or to a scale reading of $(100 - 5t)/4$ above $5t$, or to an actual scale reading of $25 + 3.75t$.

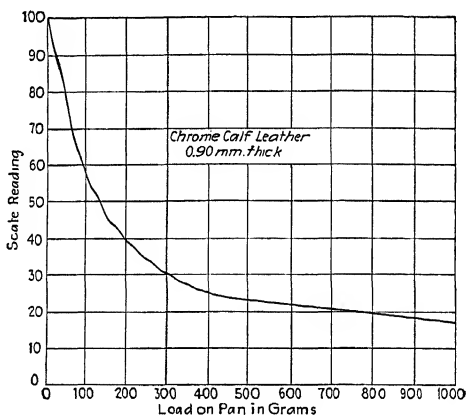


FIG. 37.—Degree of compression of a circle of leather as a function of load in apparatus for measuring temper.

In making the measurements with a strip of leather in place, weights are placed upon the pan until the scale reading is $25 + 3.75t$. The weight required is called W_1 . Its value depends not only upon the flexibility of the leather but also upon the resistance of the spiral spring. The weight required to depress the pan to give a reading of $25 + 3.75t$ with no leather is called W_2 . The weight required for the leather alone is thus given by the equation $W = W_1 - W_2$. This is called the flexibility factor, one of the elements making up the temper of the leather.

The other factor is the percentage recovery of the diameter of the circle of leather when the weights are released. Immediately

after depressing the leather to give a reading of $25 + 3.75t$, the weights are removed and then weights are again added until the pan just touches the leather and the scale reading is noted. This reading r enables one to calculate the percentage recovery R from the formula

$$R = \frac{r - 25}{0.75 - 0.0375t}$$

Temper Values for Typical Shoe-upper Leathers.—With the exception of the sole leathers, the 18 leathers described earlier in this chapter were subjected to measurements of temper, with the results shown in Table 26.

The table shows measurements for both butt and belly regions where these were available. In most cases, the flexibility factor was much less in the belly than in the butt, which is in accord with the looser structure of the belly portions. The authors were surprised not to find a greater variation in the percentage of recovery. The very low flexibility factors for kangaroo, kid, and suede are what one would expect from their behavior in wear.

TABLE 26.—TEMPER VALUES FOR TYPICAL SHOE-UPPER LEATHERS

Sample No.	Kind of leather	Thickness, millimeters		Flexibility factor, grams		Per cent recovery	
		Butt	Belly	Butt	Belly	Butt	Belly
1	Vegetable calf.....	1.20	1.20	380	285	64	64
2	Chrome calf.....	1.10	1.10	330	230	72	61
3	Glazed kid.....	0.82	0.74	113	78	65	65
4	Kangaroo.....	0.59	0.53	63	10	70	45
5	Cordovan.....	1.15	435	...	69	
6	Buck.....	0.88	0.85	100	37	80	72
7	Chrome side.....	1.30	1.20	400	130	57	49
8	Suede.....	0.70	0.95	13	14	63	58
9	Calf lining.....	0.82	0.75	285	150	67	62
10	Sheep lining.....	0.97	0.70	125	138	67	58
11	Shark.....	0.80	0.85	175	95	64	64
12	Patent side.....	1.08	1.00	135	32	60	48
13	Patent kid.....	0.94	1.06	68	52	65	65
14	Patent colt.....	1.48	1.35	300	175	57	66
15	Heavy chrome.....	2.70	1,200	...	65	
16	Chrome retan.....	2.65	2.60	950	950	54	54

Effect of Splitting—Two series of tests were made to show the effect of reducing the thickness of chrome calf leather by splitting. In each case only the grain split was tested. The results are shown in Fig. 38. Splitting reduces the flexibility factor very sharply but is practically without effect upon the recovery factor.

The flexibility factor appears to be reduced also by staking, graining, and increasing the contents of water or fat. In using the method or the figures given in this chapter, it should be remembered that the method is quite new at the time of this writing and that it may be found advisable to modify it in order to make it of greater service.

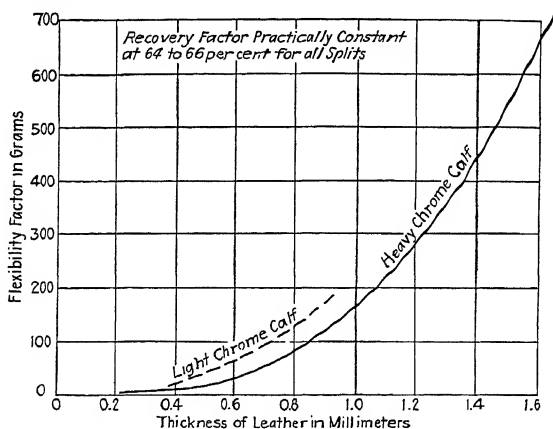


Fig. 38.—Effect of reducing thickness of chrome leather by splitting upon temper values.

RESILIENCE (42, 55)

A property closely associated with temper of leather is resilience. Temper is of greatest importance for shoe-upper leather, and resilience for sole and heel leather. A very simple apparatus, designed by Wilson (42), for measuring resilience of leather is shown in Fig. 39. It may be found convenient to use the same block and rod as that used in the apparatus for measuring temper. The calibrated glass tube may be an old burette. In the authors' tests, the brass plunger is a piece of rod weighing 48.5 g. and having a circular base of 0.70 sq. cm. In making a measurement, the plunger is allowed to drop on to the leather sample placed on

the block from a height of exactly 600 mm., and the percentage rebound of the plunger is measured by means of calibration marks on the glass tube through which the plunger is dropped. The plunger does a certain amount of work in compressing the leather when it falls upon it, and the leather then returns a certain fraction of the energy it has received, measured by the percentage rebound of the plunger, which thus becomes a measure of the resilience of the leather.

Effect of Thickness.—If the leather is immeasurably thin, the value found for resilience will be merely that of the maple block. Wilson and Kern (55) studied the effect of thickness of the sample by means of a series of slices of a pure gum rubber stopper. The results are shown in Table 27. The maple block shows a resilience of 53; that is, the plunger rebounds 53 per cent of the height from which it was dropped, or to the 318-mm. mark. With increasing thickness of the rubber, the resilience measured becomes more nearly that of the rubber itself. A minimum is reached at a thickness of 0.39 mm. and then the effect of thickness of the rubber upon its own resilience begins to play a part, the rubber becoming more resilient with increasing thickness and appearing to approach some limiting value.

In comparing the resilience of different leathers, thickness is undoubtedly a factor of considerable importance. But the resilience of any single piece of leather is apparently not the same throughout its entire thickness, so that making all samples for comparison the same thickness by means of splitting would lead to incorrect results. The more reliable way seemed to be to set the standard thickness high enough to eliminate the resilience of the block itself and to measure the resilience of different numbers of thicknesses of each sample, plot the curve for resilience as a function of thickness, and then pick off the point corresponding to the standard thickness.

Effect of Water and Fat Contents of Leather.—Previous tests have also shown that grease content and water content both markedly affect the resilience. It is thus evident that measure-

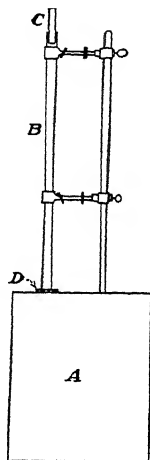


FIG. 39.—Apparatus for measuring resilience of leather. A. Solid maple block. B. Calibrated glass tube. C. Brass plunger. D. Leather sample.

TABLE 27.—RESILIENCE OF SLICES OF A PURE GUM RUBBER STOPPER AS A FUNCTION OF THICKNESS

Thickness, millimeters	Resilience
0.00	53
0.50	29
0.68	25
0.93	23
1.37	24
1.88	26
2.46	29
3.70	34
7.20	37
26.00	44

ments of different samples must be made in contact with atmospheres of the same relative humidity. Both effects are shown in Figs. 40 and 41. The sample tested is the vegetable-tanned sole leather whose analysis is given in Table 6 of Chap. II. Figure 40 shows the water content as a function of relative humidity of the atmosphere after 2 months' contact. The

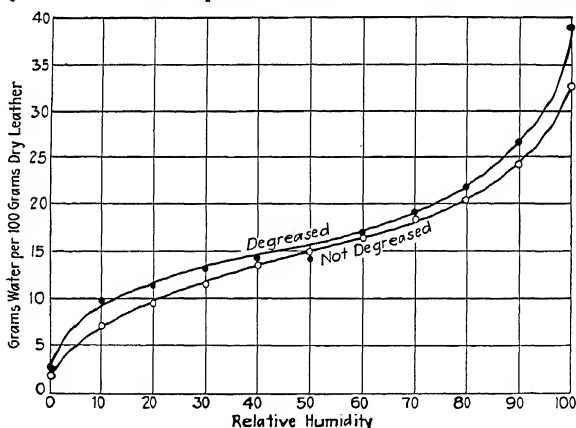


FIG. 40.—Water content of sole leather as a function of relative humidity of the atmosphere.

degreased sample absorbs a little more water than the normal samples. Figure 41 shows the effect upon the resilience. The resilience falls with increasing relative humidity and water content of the leather, and it is greater for the degreased sample than for the normal leather. The effect of thickness is eliminated

here because all samples were initially of practically the same thickness—6 mm. Degreasing the chrome sole leather raised its resilience from 17 to 34, showing that its very low resilience was due to high grease content.

Resiliency Values for Typical Shoe Leathers (55).—In measuring the resilience of the 18 leathers described above, the standard thickness was set at 3 mm. This required six thicknesses of the kangaroo leather; with each successive addition of another disk of leather beginning with one, the resilience was as follows: 37, 28, 27, 25, 25, and 24. Plotting these values against total thickness, the value for 3 mm. was 24 and was so recorded. The values for the vegetable-tanned calf were 20, 21, 22, and 23, giving a value of 22 for 3 mm. of thickness. The values for the

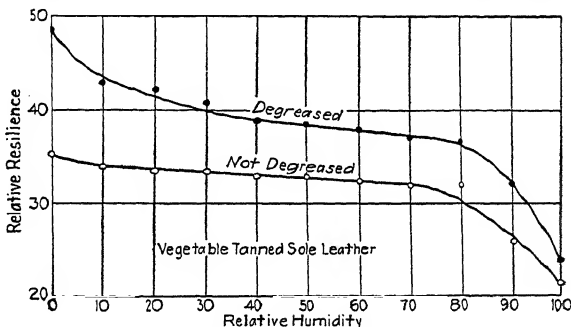


FIG. 41.—Resilience of sole leather as a function of relative humidity.

two sole leathers were measured at their normal thickness, since this was greater than 3 mm. The disks of leather for the tests were cut with a circular die 3 cm. in diameter from the butt of each skin, and they were all in equilibrium with an atmosphere of 50 per cent relative humidity. The results are given in Table 28.

The relation of resilience to the comfort of the wearer of the shoes is complicated by a number of factors not yet clearly defined. In steels, resilience is associated with hardness; but materials like rubber may be very resilient and yet quit soft. If an increase in resilience of leather is accompanied by a change in the value of some other important property, this latter may entirely mask the effect of change of resilience alone. For example, increasing water content of leather lowers its resilience, but it also lowers its resistance to deformation. The effect of

TABLE 28.—RESILIENCE OF VARIOUS LEATHERS IN TERMS OF THE PERCENTAGE REBOUND OF A PLUNGER DROPPED UPON THEM UNDER CERTAIN PRESCRIBED CONDITIONS

Sample No.	Kind of leather	Resilience
1	Vegetable calf.	22
2	Chrome calf...	26
3	Glazed kid....	28
4	Kangaroo.....	24
5	Cordovan.....	16
6	Buck.....	23
7	Chrome side..	21
8	Suede.....	21
9	Calf lining...	22
10	Sheep lining...	21
11	Shark.....	23
12	Patent side....	19
13	Patent kid....	22
14	Patent colt....	23
15	Heavy chrome	17
16	Chrome retan.	11
17	Vegetable sole.	39
18	Chrome sole...	17

the change in resistance to deformation would have to be known before one could calculate the effect of the change in resilience. It is believed that a high degree of resilience of the leather of a heel is desirable in walking, where a momentum is developed and part of the energy added to one step is carried over to the next, lessening the total exertion. However, the subject requires much further study.

BREAK

In judging the quality of leather for very fine shoe uppers or novelties, much importance is attached to the fineness of what is called the "break" of the leather. What is meant by the term will be made clear by a description of the authors' method of measuring it (45). A strip of the leather, grain side in, is drawn tightly about a glass rod 3.2 mm. in diameter so that the edge of the leather is flush with one end of the rod. A line is drawn across the end of the rod through its center. It will be noted that the grain becomes puckered or wrinkled and the number of wrinkles over half of the circumference may be counted from one end of the line to the other. This number multiplied by two

gives the number of wrinkles per centimeter. This is a quantitative measure of the break of the leather, the greater the number of wrinkles per centimeter the finer the break. A leather with 25 or more wrinkles per centimeter is said to have a fine break; one with 12, a fair break; and one with 6 or less, a coarse break. In counting the number of wrinkles, it is desirable to use a magnifying glass. Table 29 gives a series of measurements made on the butts of the 16 leathers used for measurements of temper.

TABLE 29.—BREAK VALUES FOR TYPICAL SHOE-UPPER LEATHERS

Sample No.	Kind of leather	Break in wrinkles per centimeter
1	Vegetable calf....	28
2	Chrome calf.....	28
3	Glazed kid.....	14
4	Kangaroo.....	18
5	Cordovan.....	0
6	Buck.....	0
7	Chrome side.....	18
8	Suede (grain side)	14
9	Calf lining.....	26
10	Sheep lining.....	18
11	Shark.....	0
12	Patent side.....	0
13	Patent kid.....	0
14	Patent colt.....	0
15	Heavy chrome....	12
16	Chrome retan....	0

Break values for the belly regions ranged from one-half to two-thirds of those found for the butt regions. As a rule, the authors have found calfskins to have finer breaks than any other type of skin, but this is not necessarily true. The break of a calfskin can be made very coarse by improper treatment in the tannery. The fineness of break depends upon the extent to which the fibers of the grain surface are lubricated so that they may slide easily over one another. The use of finishes that cause these fibers to stick together causes the break to become coarser and even pipy if the skin is inclined to be loose. Skins of tight structure usually have finer breaks than similar skins of looser structure. For this reason, the butt portions of a skin usually

have much finer breaks than the flank portions. For the same reason, calfskins have finer breaks than kid skins, although a kid skin with its grain well lubricated might have a finer break than a calfskin improperly finished. Kind of tannage appears to have but little effect; equally fine breaks can be produced by the chrome or vegetable tanning process. Varying combinations of the two tannages, however, may affect the break very greatly.

The buck leather showed no break because the grain surface had been buffed. The cordovan and chrome retan leathers showed no break because they were finished on the flesh side. The break value for the suede leather means nothing, because this leather is worn flesh side out. The patent leathers showed no break of the heavy varnish coats on the grain. When patent leathers become old, they often do break up to some extent. Then the break may conveniently be measured by drawing the leather around the glass rod with a motion such as is used in graining or boarding leathers and then counting the number of creases to the centimeter. Usually the break of leather is measured only in a qualitative way by pressing on the grain side with the pointer of the right hand and drawing up the leather around it with the fingers of the left hand. It is hoped that the simple method described will be found useful in making quantitative studies of break as a function of many controllable variable factors.

DENSITY

The density or apparent specific gravity of leather varies with the water content and so should always be measured at a known water content. It is best to make the measurement in connection with the chemical analysis. Cut the sample for analysis to a definite area. Then measure its average thickness and calculate the volume in cubic centimeters. Weigh the sample and record the density as the weight in grams per cubic centimeter. Then prepare the sample for analysis and place in a well-stoppered bottle before there has been any appreciable change in water content.

Mercury-displacement Method.—When only small or irregularly shaped pieces are available, the volume may be determined by measuring the volume of mercury displaced. Grassler (13) describes a convenient apparatus for making this measurement. The apparatus consists of two glass tubes connected by heavy rubber tubing. One tube, resembling a burette, is calibrated in 0.1 cc. The other, which is wide enough to admit pieces

of leather about 1 in. square, is closed by a ground-in stopper carrying a capillary tube bearing a mark. Mercury is poured into the measuring tube until the level stands at the mark on the capillary, when the volume in the measuring tube is read. By lowering the measuring tube, the mercury is partly withdrawn from the leather tube; the sample, previously weighed, is introduced; the stopper reinserted; and the measuring tube again raised until the mercury level again stands at the mark on the capillary. The level in the measuring tube is read again, and the increase in volume is taken as the volume of the leather.

A simpler, but less accurate, procedure is to submerge the leather, either piece by piece or in the form of a long strip, beneath the surface of mercury in an ordinary burette, by means of a needle. This procedure can be applied only to sole or other very stiff leather.

YIELD VALUES

Pounds of Leather per Pound of Hide Substance.—Divide 100 by the percentage of hide substance.

Square Feet of Leather per Pound of Leather.—Multiply the area of the sample in square centimeters by 0.00108, and divide by 0.0022 times the weight in grams.

Square Feet of Leather per Pound of Hide Substance.—Divide 100 times (square feet leather per pound leather) by the percentage of hide substance.

Square Feet of Leather 1 mm. Thick per Pound of Hide Substance.—Multiply (square feet leather per pound hide substance) by the thickness in millimeters.

Cutting Value (Equals Square Feet of Leather Nine Irons Thick per Pound of Leather).—Divide square feet of leather per pound of leather by 4.76, and multiply by thickness in millimeters.

References¹

1. BALDERSTON, L.: Flexing Test for Leather, *J. Am. Leather Chem. Assoc.*, **23**, 221, 1928.
2. BALDERSTON, L.: Wear Resistance of Sole Leather, *ibid.*, **11**, 429, 498, 1916; **12**, 523, 1917.
3. BERGMANN, M.: The Permeability of Hide and Leather, *Collegium*, 571, 1927; 150, 1929. BERGMANN, M., and S. LUDEWIG: Permeability of Skin and Leather to Gases, *ibid.*, 343, 1928.
4. BOWKER, R. C.: Durability of Sole Leather Filled with Sulfite Cellulose Extract, *Bur. Stand. Tech. Paper No.* 215, 1922.
5. BOWKER, R. C. and J. B. CHURCHILL: Effect of Oils, Greases, and Degree of Tannage on the Physical Properties of Russet Harness Leather, *ibid.*, No. 160, 1920.
6. BOWKER, R. C. and M. N. V. GEIB: Comparative Durability of Chrome and Vegetable-tanned Sole Leather, *ibid.*, No. 286, 1925.
7. BRADLEY, H., A. T. MCKAY, and B. WORSWICK: Moisture in Leather, *J. Intern. Soc. Leather Trades Chem.*, **13**, 10, 87, 1929.

¹C. M. Spiers has compiled an exhaustive bibliography on the physical properties of leather, published serially in *J. Intern. Soc. Leather Trades Chem.* and *J. Am. Leather Chem. Assoc.*, 1930-31.

8. CHATERS, W. J.: Effect of Heat on Wetted Vegetable-tanned Leather, *J. Intern. Soc. Leather Trades Chem.*, **12**, 544, 608, 1928; **13**, 24, 427, 1929.
9. DEFORGE, A.: Relation between Composition of Leather and Its Tensile Strength and Stretch, *Halle aux Cuirs*, 179, 1926.
10. FREY, R. W., I. D. CLARKE, and L. R. LEINBACH: Some Comparative Data on Vegetable and Chrome Retanned Sole Leather, *J. Am. Leather Chem. Assoc.*, **23**, 430, 1928.
11. GAYLEY, C. T.: Water Penetration Apparatus for Leathers, *ibid.*, **11**, 36, 1916.
12. GERSSEN, N. J.: Electrical Determination of Permeability of Leather to Water, *Collegium*, 337, 1928.
13. GRASSER, GEORG: "Handbuch für gerbereichemische Laboratorien," 3d ed., Julius Springer, Vienna, 1929.
14. GREEVES, W. S.: The Ideal Army Upper Leather, *Leather World*, **15**, 1077, 1923.
15. HART, R. W.: Laboratory Wearing Test to Determine the Relative Wear Resistance of Sole Leather at Different Depths throughout the Thickness of the Hide, *Bur. Stand. Tech. Paper No.* 166, 1920.
16. HART, R. W., and R. C. BOWKER: Apparatus for Measuring the Relative Wear of Sole Leathers, with Results Obtained for Leathers from Different Parts of the Hide, *ibid.*, No. 147, 1920.
17. HIRSCH, M.: The Hygroscopic Properties of Leather According to the Researches of Wilson, Daub, and Kern, *Collegium*, 403, 1927.
18. HUC, P.: Density of Leather, *Halle aux Cuirs*, 117, 321, 1924.
19. JABLONSKY, L.: Permeability of Leather to Water, *Collegium*, 616, 1925.
20. JALADE, E.: Determination of the Permeability of Sole Leather to Water, *Cuir tech.*, **9**, 69, 296, 372, 1920.
21. JALADE, E.: Density of Leather, *Halle aux Cuirs*, 241, 1924.
22. McCANDLISH, D., and E. G. HANDLEY: The Tensile Strength and Stretch of Vegetable-tanned Belting Leather, *Leather Trades Year Book*, 53, 1925.
23. NIHOUL, E.: Permeability of Leather, *Collegium, London ed.*, 147, 1916.
24. ORTHMANN, A. C.: Properties [Permeability] of Leather, *J. Am. Leather Chem. Assoc.*, **23**, 184, 1928.
25. PAVLOVITSCH, P.: Testing of Leather for Wear, *Collegium*, 455, 1925.
26. PORTER, R. E.: Per Cent Gravity, Per Cent Voids, and Pile-up of Leather, *J. Am. Leather Chem. Assoc.*, **24**, 36, 1929.
27. POWARNIN, G.: Physical Testing of Leather, *Collegium*, 169, 1925; 125, 1927.
28. REISNEK, A.: Volumetric Method for Determining the Water Absorption of Sole Leather, *Schweitz. Leder-ind. Ztg.*, No. 42, 1925.
29. REISNEK, A.: Measurement of Porosity of Leather, *ibid.*, No. 41, 1925.
30. ROGERS, A.: Some Suggested Tests on Shoe Upper Leather, *J. Am. Leather Chem. Assoc.*, **20**, 495, 1925.
31. ROGERS, J. S., and R. W. FREY: Volumenometer, *Ind. Eng. Chem.*, **10**, 554, 1918.
32. SMETKIN, A.: Measuring Apparatus for Determining the Elasticity of Sole Leather, *Collegium*, 378, 1925.

33. SPRAGUE, F. O.: Water Penetration Tests for Sole Leather, *J. Am. Leather Chem. Assoc.*, **24**, 87, 1929.
34. THUAU, U. J.: Wear Resistance of Vegetable-tanned Sole Leather, *Cuir, tech.*, **17**, 360, 1928.
35. V. A. G. D. A. (STIASNY, E., ed.): "Gerbereichemisches Taschenbuch" 2d ed., Theodor Steinkopff, Dresden and Leipzig, 1929.
36. VAN DER WAERDEN, H.: The Water Permeability of Sole Leather, *Collegium*, **453**, 1928.
37. VEITCH, F. P., R. W. FREY, and I. D. CLARKE: Wearing Qualities of Shoe Leathers, *U. S. Dept. Agriculture Bull. No. 1168*, 1923.
38. VEITCH, F. P., R. W. FREY, and L. R. LEINBACH: Influence of Atmospheric Humidity on the Strength and Stretch of Leather, *J. Am. Leather Chem. Assoc.*, **17**, 492, 1922.
39. WHITMORE, L. M., and G. V. DOWNING: Water Absorption and Penetration Tests for Sole Leather, *ibid.*, **23**, 603, 1928.
40. WHITMORE, L. M., R. W. HART, and A. J. BECK: The Effect of Grease on the Tensile Strength of Strap and Harness Leather, *ibid.*, **14**, 128, 1919.
41. WILSON, J. A.: "The Chemistry of Leather Manufacture," A. C. S. Mon. Ser., 2d ed., The Chemical Catalog Company Inc., New York, 1928-1929.
42. WILSON, J. A.: Comparative Resilience of Leather and Rubber Heels, *J. Am. Leather Chem. Assoc.*, **20**, 576, 1925.
43. WILSON, J. A.: Destructive Action of Sulfuric and Hydrochloric Acids on Leathers, *Ind. Eng. Chem.*, **13**, 47, 1926.
44. WILSON, J. A., *et al.*: Properties of Leather, Committee Report, *J. Am. Leather Chem. Assoc.*, **24**, 2, 1929.
45. WILSON, J. A.: Properties of Shoe Leather: VII, Temper and Break, *ibid.*, **24**, 112, 1929.
46. WILSON, J. A., and G. DAUB: Properties of Shoe Leather: IV, Strength, Stretch, and Stitch Tear, *ibid.*, **21**, 294, 1926.
47. WILSON, J. A., and E. J. DIENER: Effect of Color of Leather on Its Temperature in Sunlight, *Hide and Leather*, **73**, No. 23, 39, 1927.
48. WILSON, J. A., and A. F. GALLUN, JR.: Chemistry and Comfort; Relation between the Chemical Composition of Leather and the Comfort of Shoes Made Therefrom, *Ind. Eng. Chem.*, **16**, 268, 1924.
49. WILSON, J. A., and A. F. GALLUN JR.: Strength and Stretch of Calf and Kid Leathers as Functions of Oil Content, *ibid.*, **16**, 1147, 1924.
50. WILSON, J. A., and R. O. GUETTLER: Properties of Shoe Leather: III, Ventilating Properties, *J. Am. Leather Chem. Assoc.*, **21**, 241, 1926.
51. WILSON, J. A., and E. J. KERN: Effect of Relative Humidity on the Destruction of Leather by Acids, *Ind. Eng. Chem.*, **19**, 115, 1927.
52. WILSON, J. A., and E. J. KERN: Effect of Splitting on the Tensile Strength of Leather, *Ind. Eng. Chem.*, **18**, 312, 1926.
53. WILSON, J. A., and E. J. KERN: Properties of Shoe Leather: V, Area Change with Relative Humidity, *J. Am. Leather Chem. Assoc.*, **21**, 351, 1926.
54. WILSON, J. A., and E. J. KERN: Variations in Tensile Strength of Calf Leather with Relative Humidity, *ibid.*, **21**, 250, 1926.
55. WILSON, J. A., and E. J. KERN: Properties of Shoe Leather: VI, Resilience, *ibid.*, **21**, 399, 1926.

56. WILSON, J. A., and G. O. LINES: The Ventilating Properties of Leather, *Ind. Eng. Chem.*, **17**, 570, 1925.
57. WILSON, R. E.: Humidity Control by Means of Sulfuric Acid Solutions, with Critical Compilations of Vapor Pressure Data, *ibid.*, **13**, 326, 1921; WILSON, R. E., and T. FUWA: Humidity Equilibria of Various Common Substances, *ibid.*, **14**, 913, 1922.
58. WINANDY, P.: Determination of Value of Leather by Means of Specific Gravity, *Halle aux Cuirs*, 314, 1924.
59. WOODROFFE, D.: Wear Resistance of Vegetable-tanned Insole Bellies, *J. Intern. Soc. Leather Trades Chem.*, **10**, 266, 1926.
60. WOODROFFE, D., and D. E. GILBERT: Effect of Filling Materials on the Strength and Stretch of Sole Leather, *ibid.*, **11**, 68, 1927.
61. WORMELEY, P. L., R. C. BOWKER, R. W. HART, and L. M. WHITMORE: Effect on Glucose and Salts on the Wearing Quality of Sole Leather, *Bur. Stand. Tech. Paper No. 138*, 1919.

CHAPTER V

BACTERIAL COUNTS

Tanneries abound with microorganisms. They have been called the tanners' invisible friends and foes. Guarding the skins against damage resulting from their activity is one of the most difficult tasks the tanner is called upon to meet. Only a very inadequate start has been made in the study of these interesting forms of plant life and of their behavior in the tannery, but through intensive research we hope some day to control their activities just as accurately as it is now possible to control some of the chemical processes.

The four great subdivisions of plant life are the *Spermatophyta* or seed plants, the *Bryophyta* or moss plants, the *Pteridophyta* or fern plants, and the *Thallophyta*, which include bacteria, yeasts, and molds, the common microorganisms of the tannery.

The *Thallophyta* are simple plants which are never differentiated into roots, stems, and leaves. Those which contain chlorophyll are the *Schizophyta* or blue-green algae; those unicellular plants which multiply by cell fission only and contain no chlorophyll are known as the *Schizomycetes* or bacteria. Those unicellular or multicellular plants which multiply by means other than simple cell fission and contain no chlorophyll are the *Fungi*, which include yeasts and molds, or mildews.

Bacteria.—A *bacterium* is a plant consisting of a single cell containing no chlorophyll and reproducing only by cell fission. Bacterial cells are usually one of three shapes: spheres, straight rods, or bent rods. A spherical cell is a *coccus*; a straight rod, a *bacillus*; and a bent rod, a *spirillum*. Bacteria are so small that it is customary to take as the unit of measurement the micron, which is one-thousandth of 1 mm. The dimensions of common bacteria range from about 0.5 micron to 10 microns. A bacterium of average size might have a volume of 1 cu. micron, so it would take one trillion bacteria to fill the space of 1 cu. cm. Of all the liquors in the tannery, those most heavily laden with

bacteria are the bate liquors, and the highest count ever obtained in the authors' laboratories of a bate liquor was slightly more than one billion per cubic centimeter. This tremendous number occupies only about 0.1 per cent of the volume of the liquor and probably weighs not more than 1 mg.

Bacteria multiply by a process of cell fission. The cell grows until one dimension has practically doubled, when it separates into two individual cells. Some bacteria produce spores in the course of their growth. The spore is usually much more resistant to destruction than the parent cell and the theory has been advanced that spore formation is not a method of reproduction but rather a protection against unfavorable environment.

Buchanan (5) has made an interesting calculation of the rate of growth of bacteria under ideal conditions. Probably most of the more active bacteria can grow to their full size and divide to form two individuals within 30 min. If it is assumed that this process continues for 2 days, the number of bacteria growing from one initial cell will be 2 raised to the ninety-sixth power, and their total weight more than one trillion tons. Of course no such bacterial masses could ever be formed because of the disappearance of available food and the production by the bacteria of substances hindering their own development.

Bacterial activity involves the diffusion of dissolved foods through their cell walls, reactions within the cells, growth and reproduction, and the formation of substances which diffuse out from the cell into the solution in which the bacteria are suspended. Often these excreted materials are of very great importance. Since the collagen of skin is insoluble, it cannot diffuse into the bacterial cell, but the cell may secrete a proteolytic enzyme which will hydrolyze the collagen, forming soluble products which can diffuse through the bacterial wall and into the cell, where they help to form more of the same enzyme to diffuse out and hydrolyze more collagen. Bacterial cells of different kinds may secrete a large variety of active substances.

Bacterial Damage to Skins.—Skins must be protected against bacterial action from the moment of flaying until they are fully tanned. Freshly flayed skins quickly pick up bacteria from their surroundings, and the soluble proteins contained in the skin furnish ideal food for the proteolytic bacteria, which multiply rapidly and secrete enzymes capable of destroying the collagen fibers of the skin.

In spite of the precautions ordinarily taken, many skins suffer from bacterial damage. Although the harm occurs before the skins have been tanned, it may not be apparent until after tanning. Damages are most common on skins which have not been properly cured, skins which have been stored in too warm a room, and skins which have been kept too long in warm or dirty water. The conditions which determine the nature of the damage are, however, not well understood. There seems to be a special type of damage peculiar to each given set of conditions. For example, in some cases only the grain surface seems to be affected, in others only the regions close to the blood vessels, and in still others only the glandular region separating the thermostat and reticular layers of the skin. Examples of these have recently been illustrated by Wilson and Daub (26, 27).

The tanner is familiar with a number of general methods for retarding bacterial action. Skins that are to be kept a long time before tanning are sometimes dried; bacteria do not develop in the absence of water. In curing skins, high concentrations of salt are used, which practically stop bacterial activity.¹ In soaking skins, low temperatures are used which are unfavorable to rapid growth of bacteria. Antiseptics which destroy bacteria or inhibit their activity are sometimes employed. Another method, which promises to become of very great importance in checking bacterial action on putrescible materials is the control of pH value of the solution in contact with the putrescible materials.

Effect of pH Value.—Merrill and Fleming, in the authors' laboratories, studied the effect of pH value on bacterial damage to raw skin. In order to get liquors of definite pH value, they titrated a thirtieth-molar solution of phosphoric acid with sodium hydroxide, following the titration with the hydrogen electrode. The phosphate served as a buffer to prevent wide fluctuations of pH value after the strips of skin were introduced. These were taken from skins either after soaking or after bating and placed in solutions of definite pH value, kept at 25°C. in a thermostat. From time to time the strips of skin were examined. In the case of the soaked skins, bacterial action was measured by the ease of

¹ A very interesting type of damage is the so-called "red heat" (formation of red spots) on salted skins, which has been shown to be due to an organism that thrives in strong salt solutions.

slipping of the hair; in the case of the bated skins, by the pitting of the grain.

At pH values less than 3.0, the strips suffered from acid hydrolysis. Between 3.0 and 4.5, the acid caused a loosening of the hair, but there was no pitting and no evidence of any bacterial action. Between 4.5 and 6.5 there was no hair slipping and no pitting noticeable. Between 6.5 and 8.0 both pitting and hair slipping became marked, with a maximum action at about 7.5. The actions were quite marked after 2 days. At pH values above 8, no pitting took place. The action on the hair follicles, resulting in hair slipping, decreased gradually as the pH value rose from 7.5 to 10.5, above which it increased again, apparently due to the action of the alkali rather than of bacteria.

These experiments would indicate that there is greatest danger of bacterial damage when skins are kept in contact with solutions having pH values between 6.5 and 8.0.

MAKING BACTERIAL COUNTS

Interesting and valuable information regarding bacterial development in many tannery liquors can be obtained by making counts, using the standard methods of the American Public Health Association (1), printed below by special permission.

BACTERIOLOGICAL EXAMINATION OF WATER

I. APPARATUS

1. Sample Bottles.—A glass bottle of good quality of any size or shape may be used for the bacterial sample provided it holds a sufficient amount to carry out all of the tests required and is such that it may be properly washed and sterilized and will keep the sample uncontaminated until the analysis is made. 4- or 8-oz., ground-glass stoppered bottles of good quality glass are recommended. The stopper and neck should be covered with metal foil, the bottle wrapped in paper and placed in a box suitable for transportation.

2. Pipettes.—Pipettes may be of any convenient size or shape provided it is found by actual test that they deliver accurately the required amount in the manner in which they are used. The error of calibration shall in no case exceed 2 per cent.

3. Dilution Bottles.—Bottles for use in making dilutions should preferably be of tall form and of such capacity as to hold at least twice the volume of water actually used. Close-fitting ground-glass stoppers are preferable, but tight-fitting cotton stoppers may be used, provided due care is taken to prevent contamination and to avoid loss of volume through wetting of the stopper before mixing has been accomplished.

4. Petri Dishes.—Petri dishes 10 cm. in diameter with the side wall of the bottom at least 1 cm. high shall be used with glass or porous tops (13)

as preferred. The bottoms of the dishes shall be free from bubbles and as flat as possible so that the medium shall be of uniform thickness throughout the plate.

5. Fermentation Tubes.—A fermentation tube (3) of any type may be used provided it contains at least twice as much medium as the amount of water to be tested. The Dunham tube with inverted vial is recommended.

6. Sterilization.—Glassware, except sample bottles, shall be sterilized at a temperature not less than 160°C. for not less than 1 hr.

Sample bottles may be sterilized as above or may be sterilized in a steam autoclave at 15 lb. pressure for $\frac{1}{2}$ hr.

II. MATERIALS

1. Water.—Distilled water shall be used in the preparation of all culture media and reagents.

2. Meat Extract.—Liebig's meat extract shall be used in place of meat infusion. Other brands may be substituted for Liebig's when comparative tests have shown that they give equivalent results.

3. Peptone.—Digestive Ferments Company's, Fairchild's, or any other peptone which comparative tests have shown to give equivalent results may be used.

4. Sugars.—All sugars used shall be of the highest purity.

5. Agar.—The agar used shall be of the best quality. Much of the agar on the market contains considerable amounts of sea salts (21, 22, 25). These may be removed by soaking in distilled water and draining before use.

6. Gelatin.—The gelatin used shall be of light color, shall not contain objectionable impurities, and shall be free from preservatives. The melting point shall be such that a 10-per cent standard nutrient gelatin shall melt at 25°C. or over.

7. General Chemicals.—Special effort shall be made to have all the ingredients used for culture media chemically pure.

III. PREPARATION OF CULTURE MEDIA

1. Adjustment of Reaction.—The reaction of culture media shall be stated in terms of the hydrogen-ion concentration. (6-10, 14) Adjustment to the required hydrogen-ion concentration shall be made by one of the three following methods: (1) the use of standard buffer solutions, (2) the drop-ratio method, (3) the use of prepared buffer standards. If other methods of adjustment are used, it should be so stated in the report. The color chart should not be used. A description of the above three procedures is given in Sec. XVII of the chemical part of this book.¹ Procedures 1 and 2 are considered as standard, procedure 3 as provisional.

Examples.—Add 5 cc. of distilled water to each of two clean test tubes, similar in size, shape, and color to the tubes used for the color standards; 6- by $\frac{1}{2}$ -in. tubes are recommended. Withdraw 10 cc. of the medium to be adjusted and add 5 cc. to each of these two tubes. Then to one add 5 drops of a solution of an indicator which will adequately cover the desired pH range. (For preparation see Sec. XVII, 2, of the chemical part.)¹ Using a

¹ Standard Methods of Water Analysis, 6th ed., American Public Health Association, New York, 1925. See also Chap. VII.

comparator block, superimpose the tube containing the diluted medium plus the indicator over a tube of distilled water and superimpose the tube of diluted medium without indicator over the color standard of the pH desired. (In the case of the drop-ratio method it will be necessary to make the observations through three tubes instead of two.) Titrate the tube of diluted medium plus indicator with an accurate 1:10 dilution of an approximately normal sodium hydroxide solution until the color viewed through the distilled water tube matches the color of the pH standard as observed through the diluted medium without the indicator. Calculate the amount of normal sodium hydroxide solution which must be added to the medium to reach this reaction. After the addition and thorough mixing, check the reaction.

The final reaction for broth, gelatin, and agar shall be between pH 6.2 and 7.0. For Endo medium the final reaction after the addition of chemicals shall be pH 7.8 to 8.2. The eosin methylene blue agar does not require adjustment.

The increase in the hydrogen-ion concentration during sterilization will vary slightly with the individual sterilizer in use, and the initial reaction required in order to obtain the correct final reaction will have to be determined. This increase, however, will usually be between 0.2 and 0.4 pH.

2. Sterilization.—All media shall be sterilized in the autoclave at 15 lb. (120°C.) for 15 min. after the pressure has reached 15 lb. All air must be forced out of the autoclave by allowing live steam to stream through it for a few minutes before the pressure is allowed to rise. As soon as possible after sterilization, the medium shall be removed from the autoclave and cooled rapidly. Rapid and immediate cooling of gelatin is imperative.

Media shall be sterilized in small containers and these must not be closely packed together. No part of the medium shall be more than 2.5 cm. from the outside surface of the glass, or from the surface of the medium.

3. Clarification.—The extent to which a medium should be clarified depends upon the use to which the medium is put and will vary also according to the experience and preference of the laboratory worker. Any method of clarification is allowable which will yield a medium sufficiently clear for the detection of bacterial growth and at the same time will not remove necessary nutritive ingredients. Methods may include clarification in a centrifuge or filtration through paper, cotton, cheesecloth, or towels.

4. Nutrient Broth.—Add 3 g. of beef extract and 5 g. of peptone to 1,000 cc. of distilled water.

Heat slowly on a water bath to 65°C., stirring until dissolved.

Make up the lost weight with distilled water and adjust the reaction so that the final pH will be between 6.2 and 7.0.

Bring to a boil over a free flame, cool to 25°C., make up the lost weight with distilled water, and clarify.

Distribute in test tubes, 10 cc. to each tube, or in other desired containers.

Sterilize as directed under Sterilization.

5. Sugar Broths.—Sugar broths shall be prepared in the same general manner as nutrient broth with the addition of 0.5 per cent of the required carbohydrate. The removal of muscle sugar is unnecessary, as the beef extract and peptone are free from any fermentable carbohydrates. The

reaction of sugar broths shall be the same as that required for nutrient broth. Sterilization shall be in the autoclave at 15 lb. for 15 min. after the pressure has reached 15 lb., provided that the total time of exposure to any heat is not more than $\frac{1}{2}$ hr. If it is not possible to limit the exposure to heat to $\frac{1}{2}$ hr. or less, then a 10- or 20-per cent solution of the required sugar shall be made in distilled water and sterilized either by holding at 15 lb. pressure in the autoclave for 15 min. after the pressure has reached 15 lb. or by heating in the Arnold sterilizer at 100°C. for $1\frac{1}{2}$ hr. This solution shall then be added to sterile nutrient broth in amounts sufficient to make a 0.5-per cent solution of the carbohydrate, and the mixture shall then be tubed with proper precautions for preserving its sterility and sterilized at 100°C. for 30 min. Or it is permissible to add by means of a sterile pipette directly to a tube of sterile nutrient broth enough of the sugar solution to make the required 0.5-per cent concentration. The tubes so made shall be incubated at 37°C. for 24 hr. as a test for sterility before they are used.

6. Nutrient Gelatin.—Add 3 g. of beef extract, 5 g. of peptone, and 120 g. of gelatin (undried market product as stored in the ordinary laboratory cupboard) to 1,000 cc. of distilled water.

Heat slowly on steam bath to 65°C. until all the ingredients are dissolved.

Make up the lost weight with distilled water and adjust the reaction so that after the final sterilization the pH value will be between 6.2 and 7.0.

Bring to a boil, stirring vigorously. Make up the lost weight with distilled water and clarify.

Distribute in the desired containers and sterilize as directed under Sterilization.

7. Nutrient Agar.—Add 3 g. of beef extract, 5 g. of peptone, and 15 g. of agar (undried market product as stored in the ordinary laboratory cupboard) to 1,000 cc. of distilled water. Boil until all the agar is dissolved. Cool to 45°C. in a cold water bath, then warm to 65°C. in the same bath, without stirring.

Make up the lost weight with hot distilled water and adjust the reaction so that the pH value, after the final sterilization, will be between 6.2 and 7.0.

Bring to a boiling temperature, stirring frequently, restore the lost weight with hot distilled water, and clarify.

Distribute in the desired containers, and sterilize as directed under sterilization.

8. Endo Medium (12, 15, 16). *a. Preparation of Stock Agar.*—Add 5 g. of beef extract, 10 g. of peptone, and 30 g. of agar (undried market product as stored in the ordinary laboratory cupboard) to 1,000 cc. of distilled water.

Boil until all the agar is dissolved, and then make up the lost weight due to evaporation, with distilled water. Titrate and adjust the reaction so that the final pH value will be between 7.8 and 8.2. This agar may then be clarified sufficiently by either one of the following procedures. (Inasmuch as a 3-per cent agar is rather difficult to filter and as this particular medium does not have to be entirely free of precipitate, procedure 2 is probably the better one to employ.)

Procedure 1: Bring to boil over a free flame, stirring constantly, and filter through cotton or cloth.

Procedure 2: Place a straight-walled container holding the agar in the autoclave, and hold at 15 lb. pressure for 15 min. Shut off the steam and

let the agar stand in the autoclave until solidification is complete (overnight if possible). Remove the container from the autoclave, dump the solidified agar on clean paper, and cut off the detritus from the bottom and discard. Cut and melt the clear supernatant agar and distribute in 100 cc. or larger known quantities in flasks large enough to hold the other ingredients which are to be added later.

Sterilize in the autoclave at 15 lb. for 15 min. after the pressure reaches 15 lb. as directed.

b. Preparation of Endo Medium Plates (12, 23).—Prepare a 10-per cent solution of basic fuchsin in 95-per cent alcohol, allow to stand 24 hr., decant, and filter the supernatant fluid. This is a stock solution.

When ready to make plates, melt a known portion of the stock agar and to each 100 cc. of agar add the following ingredients in the order given, mixing thoroughly after the addition of the final reagent:

One per cent of chemically pure lactose in sterile solution, 0.5 cc. of the stock basic fuchsin solution (10-per cent alcoholic solution), and 0.125 g. of anhydrous sodium sulphite dissolved in a small amount of hot distilled water. The sulphite solution must be made up fresh each time. Mix thoroughly.

Pour plates and allow to harden in the incubator before use. Inoculate by streaking on the surface.

9. Eosin Methylene Blue Agar.—Add 10 g. of Difco peptone, 2 g. of dipotassium phosphate, K_2HPO_4 , and 15 g. of undried agar to 1,000 cc. of distilled water. Boil until all ingredients are dissolved, and make up any loss due to evaporation with distilled water. Adjustment of reaction is not necessary.

Place measured quantities (100 or 200 cc.) in flasks or bottles and sterilize in the autoclave as directed at 15 lb. for 15 min.

Just prior to using, melt stock agar and add the following ingredients to each 100 cc.:

Lactose, sterile 20-per cent solution, 5 cc.

Eosin, yellowish, 2-per cent aqueous solution, 2 cc.

Methylene blue, 0.5-per cent aqueous solution, 2 cc.

Mix thoroughly, pour into Petri dishes, allow to harden, and inoculate by streaking on the surface.

It is allowable to add all the ingredients to the stock agar at the time of preparation, place in tubes or flasks, and sterilize. Decolorization of the medium occurs during sterilization. The color returns after cooling.

10. Certified Dyes.—Certified dyes should be used in the preparation of media. If other dyes are used, the amount of dye required should be determined for each sample of dye.

11. Permissible Variations in Media.—*a.* The use of dehydrated media is permissible provided comparative tests have shown that these media give results equivalent to those secured with freshly prepared media.

b. Where large amounts of water are to be tested, the use of double or triple amounts of ingredients in the media is permitted, but after the water is added to the medium the resulting dilution of the standard medium should not be over 50 per cent.

IV. SAMPLES

1. **Collection.**—Samples for bacterial analysis shall be collected in bottles which have been cleansed with great care, rinsed in clean water, and sterilized as directed under Sec. I.

Great care must be exercised to have the samples representative of the water to be tested and to see that no contamination occurs at the time of filling the bottles or prior to examination.

2. **Storage and Transportation.**—Because of the rapid and often extensive changes which may take place in the bacterial flora of bottled samples when stored even at temperatures as low as 10°C., it is urged, as of importance, that all samples be examined as promptly as possible after collection.

The time allowed for storage or transportation of a bacterial sample between the filling of the sample bottle and the beginning of the analysis should be not more than 6 hr. for impure waters and not more than 12 hr. for relatively pure waters. During the period of storage, the temperature shall be kept between 6 and 10°C. Any deviation from the above limits shall be so stated in making reports.

V. DILUTIONS

Dilution bottles shall be filled with the proper amount of tap water so that after sterilization they shall contain exactly 9 or 99 cc. as desired. The exact amount of water can be determined only by experiment with the particular autoclave in use. If desired, the 9 cc. dilution may be measured out from a flask of sterile water with a sterile pipette.

Dilution bottles shall be sterilized in the autoclave at 15 lb. (120°C.) for 15 min. after the pressure reaches 15 lb.

The sample bottle shall be shaken vigorously 25 times, and 1 cc. withdrawn and added to the proper dilution bottle as required. Each dilution bottle after the addition of the 1 cc. of the sample shall be shaken vigorously 25 times before a second dilution is made from it or before a sample is removed for plating (24).

VI. PLATING

All sample and dilution bottles shall be shaken vigorously 25 times before samples are removed for plating. Plating shall be done immediately after the dilutions are made. One cubic centimeter of the sample or dilution shall be used for plating and shall be placed in the Petri dish first. Ten cubic centimeters of liquefied medium at a temperature of 40°C. shall be added to the 1 cc. of water in the Petri dish. The cover of the Petri dish shall be lifted just enough for the introduction of the pipette or culture medium, and the lips of all test tubes or flasks used for pouring the medium shall be flamed. The medium and sample in the Petri dish shall be thoroughly mixed and uniformly spread over the bottom of the Petri dish by tilting and rotating the dish. All plates shall be solidified as rapidly as possible after pouring and placed immediately in the appropriate incubator. Endo plates shall be made by placing 1 loopful of the material to be tested on the surface of the plate and distributing the material with a sterile wire or glass rod. Eosin methylene blue plates are made in the same manner as the Endo plates.

VII. INCUBATION

Gelatin plates shall be incubated for 48 hr. at 20°C. in a dark, well-ventilated incubator in an atmosphere practically saturated with moisture (24).

Agar plates may be used for counts made either at 20 or at 37°C. The time for incubation at 20° shall be 48 hr.; and at 37°, 24 hr. The incubator shall be dark, well ventilated and saturated with moisture. Glass-covered plates shall be inverted in the incubator. Any deviation from the above-described method shall be stated in making reports.

In making report of the water examination, the medium used for the total count shall be stated, *i.e.*, whether gelatin or agar, and the temperature of incubation given.

VIII. COUNTING

In preparing plates, such amounts of the water under examination shall be planted as will give from 30 to 300 colonies on a plate (2); and the aim shall be to have always at least two plates giving colonies between these limits. Where it is possible to obtain plates showing colonies within these limits, only such plates should be considered in recording results, except where the same amount of water has been planted in two or more plates, of which one gives colonies within these limits, while the others give less than 30 or more than 300. In such case, the result recorded should be the average of all the plates planted with this amount of water. Ordinarily it is not desirable to plant more than 1 cc. of water in a plate; therefore, when the total number of colonies developing from 1 cc. is less than 30, it is obviously necessary to record the results as observed, disregarding the general rule given above.

Counting shall in all cases be done with a lens of $2\frac{1}{2}$ diameters' magnification, $3\frac{1}{2}\times$, with a focal distance of $3\frac{1}{2}$ in. The engraver's lens No. 146 made by the Bausch & Lomb Optical Company fills the requirements and is a convenient lens for the purpose.

EXAMPLES (26)

As an example, we may take the count made on some water used for soaking a pack of salted calfskins. On the agar plates at 37°C., for all dilutions less than 1,000 times, the colonies were too numerous to count. On the plate with the dilution of 10,000 times, there were 102 colonies; on the dilution of 100,000 times, 11 colonies; and on the dilution of 1,000,000 times, only 2 colonies. Since 102 lies between the preferred numbers 30 to 300, it was chosen as official, and 102 multiplied by 10,000, the value of the dilution, gives 1,020,000, the number of organisms present in 1 cu. cm. of the original sample. But the count on the gelatin plates at 20°C. was 12,500,000, indicating that only about 8 per cent of the organisms capable of growing in gelatin at 20° were able to grow in agar at 37°. This may be due to the fact that the temperature of these soak waters never exceeds 15° in practice

and that the organisms developing at the greatest rate in the soak water were incapable of development at 37°. Incubating for a longer time had no effect. The average of counts made over a period of a year showed about 1,000,000 at 37° and 12,000,000 at 20°.

A water dosed with 44 parts of chlorine per million before the skins were soaked showed counts after soaking as follows: At 20°, the count was 28,600; and at 37°, it was 33,000, indicating that the chlorine had acted more effectively on the organisms growing at the lower temperature.

The difference in count of the same sample made at different temperatures or with different culture media is often so large as to raise the question as to just what is meant by the count. No one claims that an official count of 1,000, for example, means that the sample contains only 1,000 bacterial cells per cubic centimeter. It does mean that it contains at least 1,000, but it may contain very many more. The counts have a comparative value when made under as nearly identical conditions as possible. The chemist who would use an official method in the investigation of a practical process must understand the limitations of the method or he may be led into difficulties. This is illustrated by the work of Wilson and Vollmar (28) on the effect of salt upon the bacterial count of tannery soak waters.

Effect of Salts.—When bacterial counts were made of water used for soaking salted calfskins, much higher results were obtained by substituting sterilized water from the soaks for distilled or tap water in making the necessary dilutions. At first this was attributed to the creation of an environment more nearly like that in which the bacteria had originally developed, but further investigation showed it to be due to the salt present in the dilution water.

It was found that salts may cause either an increase or a decrease in bacterial count, depending upon kind and concentration present in the culture medium, whether added directly or carried in by the sample being tested. Where counts are used in the study of the effect of antiseptics upon bacterial life in water of variable salt concentration, it is obviously of great importance to know the extent to which the salt may vary the count. For this reason, an investigation was made of the effect of the addition of different salts to the culture medium upon the bacterial count of water used for soaking salted calfskins, and a few typical results are here given.

All counts were made by the official method of the American Public Health Association, except for deviations hereinafter noted. The soak waters whose counts are given in this paper contained an average of about 0.03 mole of sodium chloride per liter, but this was reduced to a negligible value by the dilution, before planting, with sterilized distilled water, necessary to bring the number of colonies on each plate within the required limits. Duplicate series were run in every case with the soak water diluted both 10,000 and 100,000 times before plating.

Bacto¹ nutrient agar was used as a base for the culture medium.

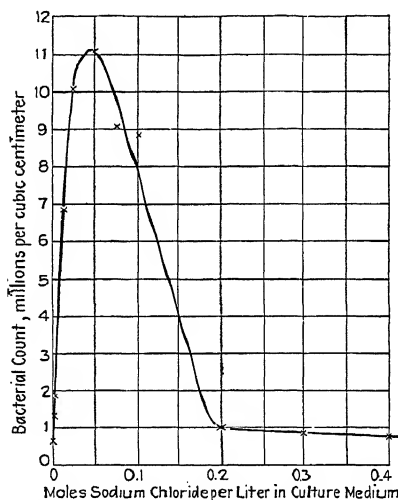


FIG. 42.—Effect of concentration of sodium chloride in culture medium upon the bacterial count of water used for soaking salted calfskins.

No attempt was made to differentiate between the combined and uncombined inorganic components of this medium, but the same sample was used in all experiments. The salts, previously dissolved in water, were added directly to the medium before making up to final volume and sterilizing. The importance of controlling the hydrogen-ion concentration was appreciated, and determinations were made in every case after incubation as well as before. In no case did the pH value lie outside the range 6.90 to 7.10. Microscopic observations were made of many pure

¹ Digestive Ferments Company, Detroit, Mich.

cultures obtained from samples of soak waters, but the variety was so great that detailed descriptions would be out of place here.

The effect of increasing the concentration of sodium chloride is shown in Fig. 42. All counts are for the same sample of soak water, the only difference being that of salt concentration in the culture medium. Using the official method, with no added salt, the count was 610,000 per cubic centimeter, but with increasing concentration of salt the count rose to a maximum of 11,100,000 at 0.05 mole per liter of added salt and then fell steadily, becoming

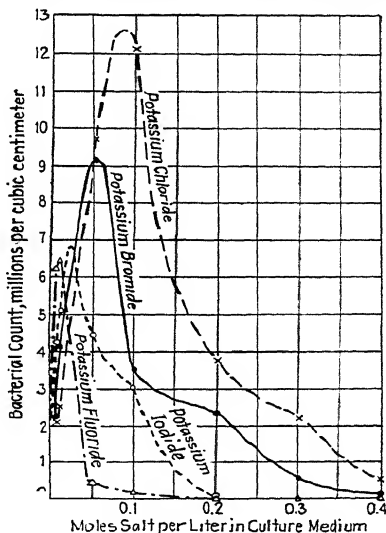


FIG. 43.—Effect of concentration of potassium halides in culture medium upon the bacterial count of water used for soaking salted calfskins.

practically zero above molar strength. The addition of 0.05 mole of sodium chloride per liter to the medium caused the appearance of eighteen times as many colonies as in the unsalted medium. That this was not due merely to an accelerated growth was indicated by the fact that incubation for a week, instead of 48 hr., did not alter any of the counts. Care was also exercised to insure against effects of manipulation in planting a large number of aliquots from the same diluted sample of soak water, by making alternate plantings in salted and unsalted media. The effect of repeated pipetting from the same sample

was a gradual increase in count in the unsalted medium from 610,000 to 960,000—quite negligible compared with the increase to 11,100,000 due to twentieth-molar sodium chloride. Numerous repetitions showed the effect to be general.

The curves in Fig. 43 furnish a comparison of the effects of the different halides of potassium upon the bacterial count of another sample of soak water. At concentrations of 0.01 mole per liter, or less, the salts all increase the count, the order of effectiveness

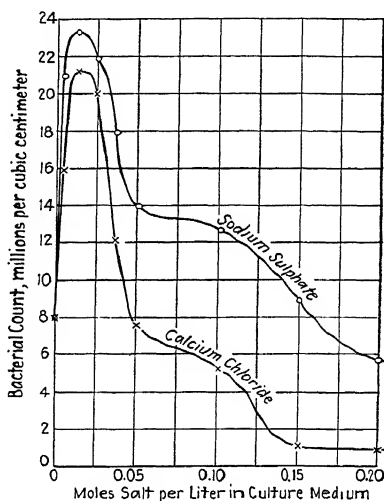


FIG. 44.—Effect of concentration of sodium sulfate or calcium chloride in culture medium upon the bacterial count of water used for soaking salted calfskins.

being fluoride > iodide > bromide > chloride. Points of maximum occur in all curves, and at higher concentrations the salts all decrease the count, the order of effectiveness being exactly the same as for increasing count at lower concentrations. Where the initial rise in the curves is steepest, the value of the point of maximum is lowest and occurs at the lowest concentration of salt.

A third sample of soak water was used to determine the effects of sodium sulfate and calcium chloride upon the count. The results are shown in Fig. 44. The general shape of all curves is the same and all seem to show curious points of inflection to the right of the point of maximum.

It was at first suggested that the effect of the salt was to produce a condition more or less favorable to the growth of certain types of bacteria, but this appeared improbable when the following facts were brought to light and considered collectively:

1. When the experiments were repeated for short portions of the curves, making successive increments of salt very small, it was found that the curves were practically continuous and that each small increment caused a corresponding increase or decrease in count.

2. Increasing the period of incubation caused no change in the number of colonies on any given plate.

3. A violent shaking of the diluted sample immediately before planting in the medium caused a large increase in count. An example of this follows: A sample shaken 15 sec. gave a count of 280,000 per cubic centimeter; 1 min., 670,000; 2 min., 1,220,000; 3 min., 1,790,000; 5 min., 2,430,000. The count was increased more than eight times simply by shaking the sample vigorously for 5 min. before planting.

A more logical explanation is that probably all the bacteria present develop upon incubation, at least in the more dilute salt solutions, but that differences in count are due to differences in the average number of bacteria (originally present in the sample) responsible for one colony on the Petri dish. The bacteria in the sample would thus be pictured as existing in groups or clusters of many individuals. The effect of a small amount of salt would be to increase the degree of dispersion of the bacteria, which would result in an increased number of colonies on the Petri dish, even though the total number of individual bacteria had not been altered by the salt; still larger amounts of salt would cause agglutination and correspondingly lower counts. Violent shaking causes an increase in count by breaking up the clusters, at least temporarily, into smaller groups.

This view likens the behavior of suspensions of bacteria to that of colloidal dispersions of simple materials, such as metallic gold, in the presence of electrolytes. Loeb (18) studied the effect of concentration of different types of ionogens upon the electrical potential difference at the surface of the particles in various kinds of colloidal dispersions. The effect of concentration of sodium chloride upon a colloidal dispersion of gold, for example, was to increase the negative potential difference to a maximum at a concentration of about 0.005 mole of sodium chloride per liter,

above which the value of the potential difference fell. Northrop and De Kruif (20), on the other hand, showed that the electrical potential difference at the surface of bacteria was markedly affected by changing concentration of electrolyte, just as in the case of colloidal dispersions. Loeb found that when the absolute value of the potential difference at the surface of particles of gold, graphite, collodion, and some other materials, in colloidal dispersion, was about 15 mv., flocculation occurred; while Northrop and De Kruif found a similar critical potential difference, about 15 mv., for the agglutination of certain types of bacteria. Still further confirmation of the view that bacteria behave toward electrolytes much like ordinary colloidal dispersions is furnished by the work of Winslow, Falk, and Caulfield (29) on the electrophoresis of bacteria.

Apparently, in both bacterial suspensions and colloidal dispersions there are opposing forces at work tending to regulate the average size of the particles, whether these be groups of bacteria or aggregates of simple molecules. Cohesive forces act to increase the size, while like electrical charges and attraction of the molecules of the particles for water tend to decrease the average size of the particles. Since it has been shown that the potential difference at the surface of bacteria is altered by change in the kind and concentration of salt, other things remaining constant, one would expect the average number of bacteria per group, and therefore the bacterial count, to be a function of the kind and concentration of salt present in the suspension, and this has been shown to be the case. It seems likely that all counts indicated in the curves are lower than the true values, and it may be questioned whether the full count of individual bacteria in a sample is ever obtained by use of the official method. In making comparative counts, the importance of maintaining constancy of pH value in the culture medium is now generally appreciated, but this work indicates that constancy of composition in other respects is also essential.

Examination of Pure Cultures.—In making bacterial counts, only the relatively huge colonies visible to the naked eye are seen. In order to view the individual organisms, special technic is required. An ordinary plate used in counting may contain a great variety of organisms, making complete identification of all organisms present in a tannery liquor a very long and tedious task. The end of a thin platinum wire is touched lightly

upon the surface of a colony in the Petri dish and then is stirred in a drop of water on a clean glass slide so as to distribute the bacteria evenly over the surface of the slide. The smear is allowed to dry in the air and then passed quickly through a flame, smear side up, two or three times to fix it. The glass slide is then dipped into a solution of the appropriate stain, washed thoroughly in running water, dried, and examined directly with the oil immersion lens. The immersion oil may be removed with xylol and the slide retained as a permanent mount.

For working details of bacteriological technic, reference must be made to the works devoted primarily to the subject (4, 5, 19).

References

1. AMERICAN PUBLIC HEALTH ASSOCIATION: "Standard Methods for the Examination of Water and Sewage," 6th ed., New York, 1925.
2. BREED, R. S., and W. D. DOTTERER: The Number of Colonies Allowable on Satisfactory Agar Plates, *J. Bact.*, **1**, 321, 1916.
3. BROWNE, W. W.: Comparative Study of the Smith Fermentation Tube and the Inverted Vial in the Determination of Sugar Fermentation. *Am. J. Pub. Health*, **3**, 701, 1913.
4. BUCHANAN, E. D., and R. E. BUCHANAN: "Bacteriology," 2d ed., The MacMillan Company, New York, 1924.
5. BUCHANAN, R. E.: "Agricultural and Industrial Bacteriology," D. Appleton & Company, New York, 1921.
6. BUNKER, G. C., and H. SCHUBER: Reactions of Culture Media, *J. Am. Water Works Assoc.*, **9**, 63, 1922.
7. CLARK, W. M.: "Reaction" of Bacteriological Culture Media, *J. Infect. Diseases*, **17**, 109, 1915.
8. CLARK, W. M., and H. A. LUBS: Colorimetric Determination of the Hydrogen-ion Concentration of Bacteriological Culture Media, *J. Wash. Acad. Sci.*, **6**, 483, 1916.
9. CLARK, W. M., and H. A. LUBS: Colorimetric Determination of Hydrogen-ion Concentration and Its Application in Bacteriology, *J. Bact.*, **2**, 1, 109, 1919.
10. COHEN, B., and W. M. CLARK: Growth of Certain Bacteria in Media of Different Hydrogen-ion Concentrations, *J. Bact.*, **4**, 409, 1919.
11. COLLINS, W. D., and H. B. RIFFENBURG: Contamination of Water Samples with Material Dissolved from Glass Container, *Ind. Eng. Chem.*, **15**, 48, 1923.
12. ENDO, S.: Method for the Detection of Typhus Bacillus, *Centralbl. Bakt. Erste Abt.*, **35**, 109, 1903-1904.
13. HILL, H. W.: Porous Tops for Petri Dishes, *J. Med. Research*, **13**, 93, 1904.
14. JONES, H. M.: Rapid Hydrogen-ion Electrode Method for the Determination of Hydrogen-ion Concentration in Bacterial Cultures or Other Turbid or Colored Solutions, *J. Infect. Diseases*, **25**, 262, 1919.

15. KENDALL, A. I., and A. W. WALKER: Isolation of *Bacillus Dysenteriae* from Stools, *J. Med. Research*, **23**, 481, 1910.
16. KINYOUN, J. J., and L. V. DEITER: Preparation of Endo's Medium, *Am. J. Pub. Health*, n.s. **2**, 979, 1912.
17. LEVINE, MAX: Bacteria Fermenting Lactose and Their Significance in Water Analysis, *Iowa State Coll. Agric. Mech. Arts, Bull.* 62, **20**, No. 31, 117.
18. LOEB, JACQUES: Influence of the Chemical Nature of Solid Particles on Their Cataphoretic P. D. in Aqueous Solutions, *J. General Physiol.*, **6**, 215, 1923.
19. MARSHALL, C. E.: "Microbiology," 3d ed., P. Blakiston's Son & Co., Philadelphia, 1921.
20. NORTHROP, J. H., and P. H. DEKRUIF: Stability of Bacterial Suspensions, *J. General Physiol.*, **4**, 639, 1922.
21. NOYES, H. A.: Agar-agar for Bacteriological Use, *Science*, n.s. **44**, 797, 1916.
22. SMITH, H. M.: Seaweed Industries of Japan, *Bull. Bur. Fisheries*, **24**, 135, 1904.
23. U. S. PUBLIC HEALTH SERVICE: Unpublished data.
24. WHIPPLE, G. C.: Necessity of Cultivating Water Bacteria in an Atmosphere Saturated with Moisture, *Tech. Quart.*, **12**, 276, 1899.
25. WHITTAKER, H. A.: Source, Manufacture, and Composition of Commercial Agar-agar, *J. Am. Public Health Assoc.*, n.s. **1**, 632, 1911.
26. WILSON, J. A.: "The Chemistry of Leather Manufacture," A. C. S. Mon. Ser., 2d ed., The Chemical Catalog Company, Inc., New York, 1928-1929.
27. WILSON, J. A., and G. DAUB: Imperfections in Leather Caused by Microorganisms, *Ind. Eng. Chem.*, **17**, 700, 1925.
28. WILSON, J. A., and C. J. VOLLMAR: Bacteria in Tannery Soak Waters, *Ind. Eng. Chem.*, **16**, 367, 1924.
29. WINSLOW, C. E. A., I. S. FALK, and M. F. CAULFIELD: Electrophoresis of Bacteria as Influenced by Hydrogen-ion Concentration, and the Presence of Sodium and Calcium Salts, *J. General Physiol.*, **6**, 177, 1923.

CHAPTER VI

MEASURING ENZYME ACTIVITY

Enzymes are used in the tannery as bating materials and to some extent as unhairing materials (15). The chief enzyme employed is trypsin, in the form of pancreatin, which is the mixed enzyme preparation obtained from the pancreas of the pig and contains also starch- and fat-digesting enzymes. The fat-digesting enzymes may play a part in operations for which the mixture is used. Proteolytic and lipolytic enzymes of vegetable origin have been proposed for bating and unhairing agents but have not thus far come into common use.

PRINCIPLES INVOLVED: CHOICE OF SUBSTRATE (20)

Since no enzyme has yet been prepared in a pure state, the only means at our command for evaluating an enzyme preparation is to measure the amount of substrate which a given amount of the sample will hydrolyze under rigidly controlled conditions. By substrate is meant the material upon which the enzyme acts; for example, casein is the substrate when this protein is being hydrolyzed by an enzyme. To facilitate the comparison of different samples, purely arbitrary units of strength are set up for each class of enzymes.

Casein is the substrate most widely used for measuring the activity of proteolytic enzymes (6, 10, 12), although gelatin is employed by many workers in this field (7). The use of casein came about because, on the one hand, it is not known with certainty which of the several proteins of the skin the enzyme is supposed to act on, nor is it easy to obtain any of these proteins in a very pure state; and, on the other, because casein is easily prepared in a high state of purity and is easy to separate from its decomposition products. There is a pretty widespread idea, also, that if two enzyme preparations digest casein at the same rate, they must of necessity digest any other protein at the same rate, though that rate may be faster or slower than their rate of digestion of casein. The authors objected to the use of casein, or any other protein not contained in skin, as the substrate for

measuring the activities of enzymes that are to be used on skin. They pointed out that trypsin acts more or less on every protein of the skin, as well as on the decomposition products of the proteins originally present. The relative activity of two different materials containing "trypsin" (18) depends entirely upon which protein is chosen as substrate. This is illustrated in Table 30. The order of activity of different specimens of trypsin, determined using elastin as substrate, is entirely different from that found using casein. Collagen gives yet a different order. Measured on keratose (19), *i.e.*, decomposition products of hair and epidermis, the order of activity is much the same as with casein. Since the removal of keratose is probably one of the most important functions of enzymes used in the tannery, the use of casein is thus to some extent justified, although this is attended by a certain amount of risk and, incidentally, offers no advantage over the use of keratose except that purified casein can be bought from supply houses while keratose must be prepared by the analyst himself. The only safe method of investigating an enzyme preparation not previously studied is to determine its activity on each one of the proteins of the skin and also its lipolytic activity. This is neither practical nor necessary in the routine examination of samples from the same source. For routine examination of enzymes that are to be used for bating, the authors recommend the use of keratose. For the testing of enzymes to be used in unhairing, a laboratory scale test of unhairing power should be carried out, employing strips of skin and maintaining the same conditions of enzyme concentration, temperature, and concentration of other materials that are to be used in practice.

In measuring the amount of work performed by an enzyme, we may start with a definite amount of substrate and a definite amount of enzyme and allow the reaction to proceed for a definite period of time. We may then determine the quantity of unchanged substrate or the quantity of products formed, either directly or by measuring some physical property that changes as a function of the progress of the reaction. Thus, if we are measuring the activity of a tryptic enzyme on casein, we can measure the amount of casein still unchanged by precipitating it at its isoelectric point, filtering, and weighing it. Or we can measure the amount of nitrogen in the filtrate, thus getting the amount of reaction product formed. If gelatin is used as

TABLE 30.—ACTIVITIES OF COMMERCIAL PANCREATINS ON DIFFERENT SUBSTRATES

Pan- creatin number	Activity upon					
	Casein (Fuld- Gross)	Casein (North- rop)	Colla- gen	Elastin	Keratose	Fat (Will- staetter)
1	3	7	4.3	40	2.4	17.2
2	7	14	3.3	11	4.2	3.4
3	22	14	1.8	10	4.5	4.0
4	33	52	6.1	17	11.5	4.4
5	60	114	12.1	25	23.3	5.2
6	83	133	13.3	20	27.3	1.8
7	167	308	31.3	20	45	4.3
8	143	30.0	0.4	80	1.4
9	333	770	38.5	50	133	0.9

substrate, the reaction may be followed by measuring the changing viscosity of the solution.

Where possible, it is preferable to determine the amount of unchanged material, since very often the first products of the reaction undergo further changes. In interpreting the data thus obtained so as to evaluate and compare different samples, three schemes have been employed:

1. Measurement of the amount of substrate acted upon in a definite time with fixed initial quantities of substrate and of the enzymes being compared.

2. Measurement of the time required for a fixed quantity of enzyme to act on a definite amount of substrate.

3. Measurement of the amount of enzyme required to hydrolyze a definite amount of substrate in a given period of time.

The first of these procedures is objectionable because the rate of reaction depends upon the concentration of the unchanged material, which is itself a variable. With a very active enzyme the reaction will proceed rapidly at first and then will slow down much more rapidly than is the case with a less active enzyme material when using the same weight of both materials. The amounts of material acted upon by the two enzymes will thus tend to approach each other the longer the time period employed. This is aggravated by the fact that the enzyme itself is frequently destroyed during the reaction and the destruction increases with the amount of reaction products formed.

While the second and third procedures are equally sound in theory, the second is less convenient if samples of very different activity are to be compared. The third is generally the best and is most frequently employed. Instead of measuring the amount of enzyme required to cause complete hydrolysis of the substrate in a given time, as is often done, it is better to measure the quantity required to act on a definite fraction of the substrate, say 40 per cent. During the first part of the reaction, the classical laws of chemical kinetics are followed with fair accuracy, but during the later stages the operation of these laws is masked by many disturbing factors, such as the combination of the enzyme with the reaction products, successive reactions, reverse actions, etc.

The activity of the enzyme is inversely proportional to the time required to bring about the decomposition of a definite amount of substrate or to the quantity of enzyme required to bring about the specified change in a definite time. In the methods which we have adopted for estimating the activity of enzymes on casein and keratose, we have expressed activities in terms of the fraction $1/hg$, where h is the number of hours required for the specified change and g is the number of grams of the enzyme sample per liter. The value of g is made great enough to bring about the specified change in reasonable time, and h is the independent variable. Difficulties involved in working with the insoluble substrates collagen and elastin have made it more suitable to fix h arbitrarily and to make g the independent variable, the activity then being measured by the fraction $1/g$.

Lipolytic activity is measured by the amount of enzyme required to hydrolyze a given amount of oil in a given time.

It is extremely important to maintain constant temperature and pH value during the course of these reactions and we have selected a temperature of 40°C. and pH value of 7.9, this being in the range of greatest activity for the pancreatic enzymes and also in the range found in practical bating. Control of pH value is effected by the use of buffer salts. With insoluble substrates requiring agitation, it is essential that the amount of agitation be made the same in all determinations. It is also necessary to preclude bacterial action by the use of suitable antiseptics. Some substrates may be hydrolyzed to some extent in the absence of the enzyme; in such cases, blanks without enzyme must be run and corrections made accordingly in the tests with enzyme.

KERATOSE (19, 20)

The keratose digesting power of an enzyme or bating material is defined as the reciprocal of the time in hours required for 1 g. of the enzyme to digest 40 per cent of 2.00 g. of keratose dissolved in 1 l. of aqueous solution at 40°C. and pH = 7.9.

Preparation of Keratose Solution.—Digest 100 g. of washed white calf hair with 100 cc. of twice-normal sodium hydroxide at 25°C. for 18 hr. Then add hydrochloric acid slowly until the pH value has been reduced to about 8; the end point can be ascertained closely enough by spotting on a tile with phenol red and thymol blue indicators. Filter through folded Swedish filter paper.

Add dilute hydrochloric acid to the filtrate, with stirring, until a copious, permanent, white precipitate forms, but be careful not to add more than enough acid to get this precipitate. Then add 200 cc. of buffer solution No. 2 (see below). Stir thoroughly and pour into a tall cylinder. Allow the precipitate to settle and test the supernatant liquid for complete precipitation by adding more of buffer solution No. 2. Continue to add the buffer until precipitation is complete. Keep the mixture cold, preferably in a refrigerator. Allow the precipitate to settle and wash 3 times by decantation.

Suspend the precipitate in about 200 cc. of water and add normal sodium hydroxide gradually and with stirring until the pH value of the solution is 8.0, as shown by spotting with the indicators. Keep stirring and add more sodium hydroxide if necessary to maintain a pH value of 8.0 until all of the keratose has passed into solution. Then transfer to a stoppered bottle, add a crystal of thymol, and keep in the refrigerator until required for use.

Buffer Solution No. 1.—Make up to 2,000 cc. an aqueous solution containing 61.7 g. of disodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 60.7 g. of sodium citrate, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5.5\text{H}_2\text{O}$, 10.3 g. of boric acid, and enough sodium hydroxide or hydrochloric acid to make a final pH value of 8.0. One hundred cubic centimeters of this solution in a liter of digestion mixture will maintain practical constancy of pH value during the digestion.

Buffer Solution No. 2.—Make up to 2,000 cc. 60 g. of acetic acid and enough sodium hydroxide to give a final pH value of 3.6. When 50 cc. of this solution is added to 100 cc. of digestion mixture containing 10 cc. of buffer solution No. 1 and 0.2 g. of keratose, the pH value is brought to 4.1, the isoelectric point of keratose and the point at which it is precipitated.

Digestion Mixture.—Determine the concentration of keratose in the stock solution as follows: Pipette 10 cc. of the stock solution into 80 cc. of water and 10 cc. of buffer solution No. 1. Add 50 cc. of buffer solution No. 2 and allow the precipitate which forms to settle for 30 min. and then filter through a Whatman No. 40 filter paper which has previously been dried at 100°C., desiccated and weighed. Wash the precipitate four times with very dilute hydrochloric acid (0.00025-normal). Dry the filter paper and residue in the oven at 100°C. overnight, transfer to a stoppered weighing bottle, cool in a desiccator, and weigh.

Pipette a volume of the keratose solution containing exactly 2 g. of keratose into a liter flask, add 100 cc. of buffer solution No. 1, dilute to about 950 cc., and warm to 40°C. Weigh off a quantity of the enzyme sample sufficient to digest 40 per cent of the keratose, that is, 0.8 g., in from 1 to 3 hr. If the first guess as to quantity to take is far out, the test should be repeated with a proper amount. As a first approximation, one may take 1 g. of ordinary commercial bating materials, 0.1 g. of U. S. P. pancreatin, or 0.01 g. of highly purified enzyme. Dissolve the enzyme in 25 cc. of water at 40°C., add to the keratose solution in the flask, and make up to exactly 1,000 cc. Keep the flask in a thermostat at 40° and count time from the moment of adding the enzyme.

Withdraw aliquots of 100 cc. each from the flask after the lapse of definite periods of time, say 0.25, 0.5, 1.0, 1.5, 2, 3, and 4 hr. Immediately upon the withdrawal of an aliquot, add to it 50 cc. of buffer solution No. 2, allow the precipitate to settle for 30 min., filter through a tared paper, wash with dilute hydrochloric acid, dry, and weigh, as described above. This gives the weight of the undigested fraction of the keratose plus a small amount of insoluble matter from the enzyme.

Corrections.—To correct for the insoluble material in the enzyme, make up a second liter of enzyme solution as described above, but leave out the keratose. Withdraw 100 cc. and treat exactly as for the 100-cc. aliquots from the digestion mixture. Deduct the weight of residue found from the weight of each residue from the digestion mixture. Often this deduction is so small that it can be ignored. So long as the time of digestion is kept within 3 or 4 hr., it is not necessary to make any correction for keratose digested in the absence of enzyme.

Calculation of Activity.—The amount of keratose digested at the end of any given time period, per 100 cc., is the difference between the weight originally present and that found in the residue after the given digestion period, a correction being made where necessary for the insoluble matter introduced in the enzyme. The percentage of the total keratose digested is then plotted as a function of time. For example, with one sample of a commercial pancreatin, the following results were obtained:

Time of digestion, hours	Grams of residue, corrected	Per cent digested
Initial	0.2020	None
0.25	0.1807	10.54
0.50	0.1625	19.55
0.90	0.1350	33.22
1.50	0.1114	45.40
2.95	0.0775	61.98

These figures are plotted in Fig. 45. The next step is to find the number of hours required to digest 40 per cent of the keratose. The 40 per cent line is drawn to the point where it intersects the smooth curve drawn through the plotted points, and from the point of intersection a perpendicular is dropped to the horizontal axis, indicated in Fig. 45 by dotted lines. The perpendicular corresponds to a time period of 1.2 hr. In this digestion, we took 0.2 g. of the enzyme per liter. Therefore $g = 0.2$ and $h = 1.2$, and the activity of the enzyme on keratose is $1/hg = 4.17$.

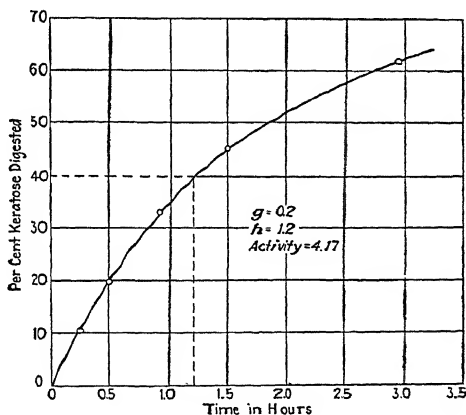


FIG. 45.—Digestion of keratose by a commercial pancreatin as a function of time. Chart showing method employed in measuring the activity of the enzyme on keratose.

The amount of enzyme and the time periods should be so chosen that at least two points are obtained on each side of the 40 per cent digestion point.

ELASTIN (16, 17, 20)

The elastin-digesting power of an enzyme is defined as the reciprocal of the number of grams of the enzyme per liter required to remove all of the elastin fibers from calfskin in 24 hr. at 40°C. and pH = 7.9.

As a buffer solution a large reservoir of sodium phosphate is kept on hand whose composition is equal to that of a fiftieth-molar solution of phosphoric acid with enough added sodium hydroxide to make the pH value 7.9. About 10 bottles of this solution are taken, each holding about 500 cc. These form a series in which increasing amounts of the enzyme sample are dissolved. The temperature is raised to 40°C. and into each is placed a

strip of limed, unhaired, and washed calfskin about 2.0 by 0.5 in. The bottles are kept in a thermostat at 40° for 24 hr., with occasional shaking. At the end of this time, the strips from all bottles, suitably marked, are washed in running tap water for 1 hr. and then put into 80-per cent alcohol. After 1 day they are transferred to 95-per cent alcohol and after another day to absolute alcohol. After about 12 hr. this is replaced by fresh absolute alcohol, and after another half day this is replaced by a mixture of equal volumes of absolute alcohol and xylene. This, in turn, is replaced after 12 hr. by a mixture of 1 volume of melted phenol and 3 volumes of xylene; and this, after another 12 hr., by pure xylene. After 12 hr. this is replaced by fresh xylene and after another half day the strips are soaked in five changes of molten paraffin about 1 hr. apart. They are then imbedded in paraffin blocks and put into the microtome for sectioning.¹

Sections are then cut at 30 microns, fixed to microscope slides, rinsed in turn with xylene, absolute alcohol, and 95-per cent alcohol, and then left for 2 hr. in Weigert's stain diluted 1:4. Then the slide is rinsed in turn with 95-per cent alcohol, phenol-xylene, and xylene. A drop of Canada balsam is placed on the section and it is then covered with a cover glass and is ready for examination under the microscope. The elastin fibers where present are stained a deep blue which makes it easy to follow their removal by the enzyme.

The strength of the enzyme is calculated from the value of the lowest concentration of enzyme which has removed all of the elastin from the skin in 24 hr. It may happen that the concentration intervals were taken too far apart to permit an accurate measure of activity. For example, suppose that 0.4 g. per liter of enzyme removed all of the elastin but that the next weaker enzyme solution tested contained only 0.1 g. per liter. The activity is measured by the fraction 1/g. In this case it would be possible to say only that the activity lies between 2.5 and 10.0. If it were desired to get the activity accurate to one unit, it would be necessary to start a second series with the following concentrations, in grams per liter: 0.111, 0.125, 0.143, 0.167, 0.200, 0.250, and 0.333. In order to get the activity of any enzyme accurate to a single unit, it will rarely require more than two series of 10 each.

Illustrations of this procedure, with photomicrographs of elastin fibers and other helpful details, may be found in Wilson's book (15).

COLLAGEN (13, 20)

The collagen-digesting power of an enzyme is defined as the reciprocal of the concentration of enzyme in grams per liter

¹ For details of technic, see Chap. III.

required for the digestion of 20 per cent of 5 g. of purified hide powder suspended in a liter of aqueous solution at 40°C. and pH = 7.9, in 3 hr.

Purification of Hide Powder.—The hide powder for this determination is prepared from standard hide powder as follows: Place 1 lb. of hide powder in a jar and cover with 7 l. of distilled water. Agitate occasionally for half a day and then dump the mixture into a large cheesecloth and squeeze out as much water as possible. Return the powder to the jar and repeat the operation until the powder has had five changes of water. It is then treated in a similar manner twice with 40 fl. oz. of 95-per cent alcohol, twice with 40 fl. oz. of a mixture of equal parts of 95-per cent alcohol and xylene, and once with 40 fl. oz. of pure xylene. After the xylene wash, the powder is allowed to remain in a current of warm air until free from the odor of xylene. The product is free from easily soluble nitrogenous matter and from fat. About 15 oz. of the purified product can be obtained from a pound of the original hide powder.

With insoluble protein fibers, like hide powder, the rate of hydrolysis by enzymes is influenced by the specific surface exposed. In order to keep this as uniform as possible, the hide powder is sifted through screens, and that portion only is used which passes a 20-mesh screen but is retained by a 40-mesh screen.

The hide powder is kept in a stoppered bottle to prevent wide changes in moisture content. It is analyzed for water and for collagen, which is taken as 5.62 times the nitrogen content. In all determinations an amount of hide powder representing exactly 0.500 g. of collagen is used with 100 cc. of digestion mixture.

Procedure.—Into each of 15 stoppered bottles put hide powder containing exactly 0.500 g. of collagen. Add to each bottle 10 cc. of buffer solution No. 1 (see under Keratose) and 40 cc. of water, and a crystal of thymol or a drop of toluol to prevent bacterial action. Keep the bottles in a thermostat at 40°C. for 1 hr. Take bottle 15, add to it 50 cc. of water, mix, and filter. Determine the amount of nitrogen in the filtrate, and calculate as the amount of collagen dissolved during the preliminary soaking. In the example to be cited this filtrate contained nitrogen equivalent to 10 mg. of collagen, from which it was concluded that each bottle contained $500 - 10 = 490$ mgm. of collagen at the end of the preliminary soaking.

Dissolve two 0.1-g. portions of enzyme in a small quantity of water. One portion, to be used for the blanks, is inactivated by boiling for 15 min. Each portion is then made up to exactly 100 cc. Into bottles 1 to 7, immediately after the preliminary soaking of 1 hr., place increasing amounts of the active enzyme solution and water to make the total volume 100 cc. Into bottles 8 to 14 place the same respective quantities of the inactivated enzyme solution and water. The quantities of enzyme taken are varied so as to cover a considerable concentration range. In the example to be cited we added to bottles 1 to 7 the following quantities of enzyme: 0.5, 1, 3, 5, 7, 10, and 20 mg. If the results of the first series indicate that the enzyme concentrations used did not cover the critical range sufficiently well, a second series may be run.

At the moment of mixing the enzyme solution and the water with the liquor containing the hide powder, all three components must be at 40°C., and the bottles must be kept in a thermostat at 40°C. during the digestion. Start counting time from the moment the enzyme was added, and remove all the bottles after exactly 3 hr. Upon removing each bottle, start filtering immediately through a dry filter, returning the filtrate until it comes through practically clear. Determine the amount of nitrogen in the filtrate, and calculate as collagen (nitrogen $\times 5.62$).

Now plot the results as a function of concentration of enzyme. This is illustrated for a special test in Fig. 46. The top curve gives the number of milligrams of nitrogen as collagen found in the filtrates from the active

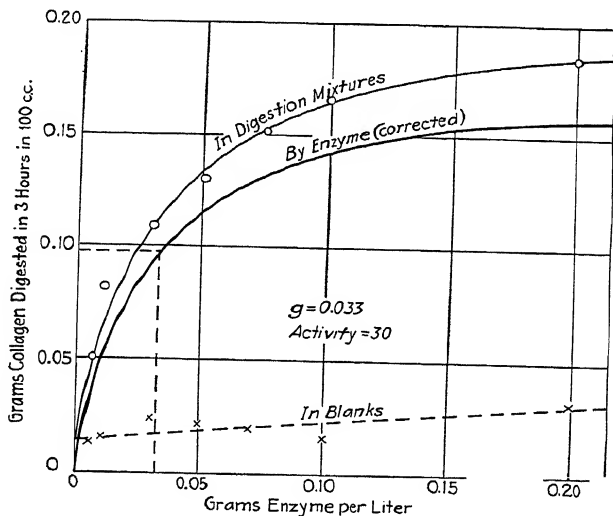


FIG. 46.—Digestion of purified hide powder by a commercial pancreatin as a function of concentration of enzyme. Chart showing method employed in measuring the activity of the enzyme on collagen.

enzyme solutions, and the crosses the number found in the filtrates from the inactivated enzyme mixtures. The amount of collagen digested by the enzyme itself is represented by the differences between these two curves, shown by the heavy continuous line. It should be noted that subtraction of the blank values from the digestion mixture values makes the necessary correction for the nitrogen introduced with the enzyme as well as that digested in the preliminary soaking period of 1 hr.

The activity of the enzyme on collagen is obtained from the corrected enzyme curve. The initial amount of collagen present upon adding the enzyme was 490 mg., and 20 per cent of this is 98 mg. By drawing lines as shown in the figure, it will be seen that a digestion of 98 mg. occurs at an enzyme concentration of 0.33 g. per liter. The activity then equals $1/0.33 = 1/0.33 = 30$.

CASEIN (20)

Numerous procedures have been devised for measuring the casein-digesting power of enzymes. In Northrop's method (8), the undigested casein is precipitated and weighed, just as in the determination of keratose-digesting power. The widely used Fuld-Gross procedure makes use of the same principle, but the digestion is carried to completion, and the end point is determined by failure of a precipitate to form upon acidification of the test solution. This method is valuable only for purposes of orientation. Several authors determine the fraction of casein that has been digested by titrating the amino acids formed. Such a method has recently been described by Schneider and Vlcek (10).

The determination of enzyme strength of commercial bates, using casein as substrate, has recently been investigated quite thoroughly by Boidin (2), in behalf of the International Society of Leather Trades Chemists. He found that precipitation of undigested casein is complete at pH about 4.6 but that, as no casein is redissolved with decreasing pH value until a pH value of 2.5 is reached, it is best to precipitate the casein at a pH value between 3 and 4 to be on the safe side. Regarding pH regulation, he found that the optimum pH value for digestion is 8.0, for pancreatic trypsin. Phosphates employed as buffers are claimed to retard digestion and to be difficult to wash out of the precipitated casein. A solution of casein dissolved in enough sodium hydroxide to give a pH value of 7.6 to 7.8 is in itself a sufficiently good buffer to maintain the pH value constant during digestion to within 0.1 to 0.2 pH unit. A digestion period of 1 hr. was recommended. The products of hydrolysis of casein were found to interfere with the precipitation of unaltered casein: 14 parts of unaltered casein, when mixed with 84 parts of completely hydrolyzed casein, could not be precipitated at all by adding acid to the solution. This is an additional argument against the Fuld-Gross method, or any method in which *complete* digestion of the substrate is taken as the end point.

Fuld-Gross Method.—This method measures the number of milligrams of enzyme required to digest completely 10 mg. of casein in exactly 1 hr. Results are expressed in Fuld-Gross units in which a value of 100 indicates that 1 mg. of enzyme can digest 100 mg. of casein in just 1 hr.

Procedure.—Dissolve 100 mg. of casein prepared according to Hammarsten,¹ in 2 cc. of twentieth-normal sodium hydroxide with the aid of gentle heating and dilute to 50 cc. with water. Dissolve 100 mg. of the enzyme in water and dilute to 500 cc. Pipette 5 cc. of casein solution into each of 10 test tubes. To successive tubes add the following volumes of enzyme solution and then water from a burette to make a final volume of 10 cc.: 0, 0.2, 0.4, 0.7, 1.0, 1.5, 2.0, 2.5, 3.0, and 5.0 cc. Shake and keep in the thermostat at 40°C. for 1 hr.

Make up a solution of 50 cc. of glacial acetic acid and 45 cc. of water. After the tubes have been digesting exactly 1 hr., add 3 drops of this acid mixture to each. The formation of a precipitate indicates the presence of some casein still undigested. If all tubes give a precipitate, the test must be repeated using higher concentrations of enzyme; if no tube gives a precipitate, the test must be repeated using lower concentrations of enzyme.

The activity of the enzyme is measured by the lowest concentration which will digest all of the casein in the hour. Thus, in a given test, upon the addition of the acid mixture, precipitates formed in tubes 1, 2, and 3 but not in the others. Tube 4 thus represented the lowest concentration of enzyme which would digest all of the casein in an hour and it contained 0.7 cc. of the enzyme solution or 0.14 mg. The activity in Fuld-Gross units equals the ratio of casein to enzyme, or $10 \div 0.14 = 71$. A closer approximation to the true value is then obtained by running a second series of 10 with closer concentration intervals ranging from that of tube 3 to that of tube 4.

The Fuld-Gross method has two outstanding points of weakness. The more serious is that it does not provide for control of pH value during the digestion. Another weakness is that its end point is that of total digestion of the casein, whereas, as we have already pointed out, it is preferable to take as end point some fraction of the total digestion, say 40 per cent.

Northrop Procedure.—The method we have found most satisfactory is that based upon a procedure described by Northrop (8). It is almost exactly the same as the procedure described above for keratose, but with the following changes: The stock solution is prepared by dissolving several grams of pure casein in 100 cc. of buffer solution No. 1 and 900 cc. of water. Undigested casein is precipitated by the addition of a sodium acetate-acetic acid buffer solution of pH = 4.1 so as to make a final pH value of 4.7, the isoelectric point of casein. Washing is carried out with 0.00015-normal hydrochloric acid. The activity is expressed as the value 1/hg, exactly as for keratose. A comparison of results between this and the Fuld-Gross method is given in Table 30.

For sale by chemical supply houses.

LIPOLYTIC ACTIVITY

Apparently no critical work has been done upon the action of lipase on the fat contained in skin during bating or unhairing with pancreatin. Since natural skin fat is difficult to obtain in quantities sufficient for enzyme-testing purposes, the method employed for determining lipolytic activity makes use of olive oil as substrate. It must be borne in mind that the relative activities of different enzymes on skin fat may be quite different from their relative activities on olive oil. Of the numerous procedures employing olive oil, that of Willstaetter, Waldschmidt-Leitz, and Memmen (14) appears to be the best.

Lipolytic activity of an enzyme is measured by the fraction $1/g$, where g is the number of grams of enzyme required to hydrolyze 24 per cent of a 2.5-g. sample of olive oil in 1 hr. under the prescribed conditions.

Procedure.—Into each of 7 small, glass-stoppered bottles weigh exactly 2.50 g. of pure olive oil (saponification value = 185.5), and add 12 cc. of the following buffer solution: 670 cc. of tenth-normal ammonium chloride, 330 cc. of tenth-normal ammonium hydroxide, and 200 cc. of water. In succession, add to the 7 flasks the following amounts of the enzyme: none, 0.01, 0.02, 0.05, 0.10, 0.15, and 0.20 g. The flask with no enzyme serves as the blank. Immediately after adding the enzyme, shake by hand for 3 min., and then keep in the thermostat at 40°C. for exactly 57 min., making a total time of contact of oil and enzyme of 1 hr.

At the end of the hour, pour the contents of each flask into a titrating vessel, rinsing out the flask with 50 cc. of a mixture of 5 parts of neutral alcohol and 1 part of neutral ethyl ether. Add 10 drops of 1-per cent alcoholic phenolphthalein, and titrate with tenth-normal sodium hydroxide to the first permanent pink color.

In this titration, alkali is consumed by the following:

1. Free fatty acid liberated by enzyme.
2. Free fatty acid in original oil.
3. The buffer material.
4. The enzyme itself.

It is the quantity of the first of these that we need to calculate the lipolytic activity. From the total titration, we must subtract the others. The second and third are constant for all members of the series and are eliminated from the calculation in the subtraction of the blank. The correction for the enzyme is found by titrating a solution containing 500 mg. of enzyme with tenth-normal sodium hydroxide. In the test cited as an example, 500 mg. of enzyme consumed 4.7 cc. of tenth-normal sodium hydroxide, making a correction of 0.0094 cc. per milligram of enzyme.

It is also necessary to know what titration would result from complete hydrolysis of the oil. This is obtained by dividing the Koettstorfer saponification number, obtained in the usual way,¹ by the ratio $5.61:2.5 = 2.244$.

¹ See Chap. XI.

The number of milligrams of potassium hydroxide equivalent to 1 cc. is 5.61, and 2.5 is the weight of oil in the test. The titration of total fatty acid thus equals $185.5:2.244 = 82.7$ cc. The ratio of the corrected titration for the digestion mixture to 82.7 cc. gives the fraction of oil hydrolyzed by the enzyme.

The following gives an example:

Milligrams enzyme	Gross	Less blank	Corrected for enzyme (<i>t</i>)	Per cent hydrolyzed ($100t \div 82.7$)
None	7.6	0.0	0.0	0.0
10	9.0	1.4	1.4	1.7
50	11.7	4.1	3.6	4.4
100	18.5	10.9	10.0	12.1
200	30.8	23.2	21.3	25.7
500	44.0	36.4	31.7	38.3

Values for percentage hydrolyzed are now plotted against milligrams of enzyme and a smooth curve drawn. A point is marked on the curve corresponding to a digestion of 24 per cent. This occurs at 0.19 g. of enzyme. Therefore the lypolytic activity is $1/g = 5.2$. In this, as well as in the other methods described, the accuracy may be increased to any desired extent by repeating the test and using closer intervals of enzyme strength.

References

1. BAYLISS, W. M.: "The Nature of Enzyme Action," 5th ed., Longmans, Green and Co., New York, 1925.
2. BOLDIN, ALBERT: Determination of the Strength of a Bate, *J. Intern. Soc. Leather Trades Chem.*, **12**, 614-625, 1928.
3. EULER, H. VON: "Chemie der Enzyme," 3d ed., J. F. Bermann, Munich, 1925.
4. FALK, K. G.: "The Chemistry of Enzyme Action," 2d ed., A. C. S. Mon. Ser., The Chemical Catalog Company, Inc., New York, 1924.
5. HOLLANDER, C. S.: Studies of the Strength of Proteolytic Enzymes in the Process of Bating, *J. Am. Leather Chem. Assoc.*, **17**, 638, 1922.
6. KUBELKA, V., and J. WAGNER: Proposed Method for the Determination of Enzymatic Value of Artificial Bates, *Gerber*, **73**, 83, 95, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 536, 1926; Casein Test as a Method for Evaluating Enzymatic Bates, *Gerber*, **69**, 80, 85, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, **23**, 70, 1928.
7. LEPETIT, R.: A Method for Determining the Practical Value of Bates, *Cuir*, **13**, 250, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 614, 1924.
8. NORTHROP, J. H.: Mechanism of the Influence of Acids and Alkalies on the Digestion of Proteins by Pepsin and Trypsin, *J. General Physiol.*, **5**, 263, 1922.
9. OPPENHEIMER, O., and R. KUHN: "Lehrbuch der Enzyme," 5th ed., George Thieme, Leipzig, 1927.

10. SCHNEIDER, J., and A. VLCEK: Objections to the Kubelka-Wagner Method for Evaluation of Enzymatic Bates, *Gerber*, 45, 1927; Titration Method for Evaluation of Enzyme Bates, *Collegium*, 342, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, 24, 58-59, 1929; Influence of Salts and Temperature on the Results of Enzyme Analysis; Method for the Investigation of Enzymatic Bates Containing NH_4Cl and NaCl , *Collegium*, 22, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, 24, 152, 1929.
11. STIASNY, E., ed.: "Gerbereichemisches Taschenbuch," 2d ed., pp. 58-59, Theodor Steinkopff, Dresden and Leipzig, 1929.
12. THOMAS, A. W.: Estimation of Tryptic Activity of Bating Materials, *J. Am. Leather Chem. Assoc.*, 15, 221-228, 1920.
13. THOMAS, A. W., and F. L. SEYMOUR-JONES: Hydrolysis of Collagen by Trypsin, *J. Am. Chem. Soc.*, 45, 1515-1522, 1923.
14. WILLSTAETER, R., E. WALDSCHMIDT-LEITZ, and F. MEMMEN: Pancreatic Enzymes: I. Determination of Pancreatic Fat Hydrolysis, *Z. Physiol. Chem.*, 126, 93, 1923.
15. WILSON, J. A.: "The Chemistry of Leather Manufacture," 2d ed., 1, 320-384, A. C. S. Mon. Ser., The Chemical Catalog Company, Inc., New York, 1928.
16. WILSON, J. A.: The Mechanism of Bating, *Ind. Eng. Chem.*, 12, 1087, 1920.
17. WILSON, J. A., and GUIDO DAUB: A Critical Study of Bating, *Ind. Eng. Chem.*, 13, 1137, 1921.
18. WILSON, J. A., and H. B. MERRILL: Activities of Pancreatic Enzymes Used in Bating on Different Substrates, *J. Am. Leather Chem. Assoc.*, 20, 50-53, 1926.
19. WILSON, J. A., and H. B. MERRILL: Another Important Rôle Played by Enzymes in Bating, *Ind. Eng. Chem.*, 18, 185, 1926.
20. WILSON, J. A., and H. B. MERRILL: Methods for Measuring the Enzyme Activities of Bating Materials, *J. Am. Leather Chem. Assoc.*, 21, 2-18, 1926.
21. WOHLGEMUTH, J.: "Crundriss der Fermentmethoden," 102, 1913.

CHAPTER VII

MEASURING pH VALUE

The determination of hydrogen-ion concentration, usually expressed as pH value, is required in the analysis of almost every sort of tannery liquor, particularly vegetable tan liquors (Chap. IX), chrome-tanning materials and liquors (Chap. X), soak, lime, and bate liquors (Chap. VIII), and fat liquors (Chap. XI). Since the determination of pH value is of such widespread application, and since the methods for determining pH are still not so familiar as the older methods of chemical analysis, it is thought desirable to devote a special chapter to the subject. It is not within our province to discuss the theory of hydrogen-ion concentration, except in an elementary way nor to describe the technic required for very precise measurements, such as are required in doing original physicochemical research. Experience has shown that men with no formal training in physical chemistry can learn quickly to make accurate and useful pH measurements, if they are provided with the proper equipment and forewarned against possible sources of error. This chapter is intended to furnish no more than an elementary statement of what hydrogen-ion concentration is, how it is expressed, and how it is determined for the purpose of controlling industrial materials. It is highly desirable that the analyst, and particularly those directing analytical work, should acquire a much broader knowledge of the subject. This can be obtained from textbooks on physical chemistry, and especially from Clark's "Determination of Hydrogen Ions" (11).

The total acidity of a solution—say a tenth-normal solution of hydrochloric acid—is its total content of substance capable of neutralizing a base. According to the ionic theory, the neutralization of an acid by a base consists of the union of hydrogen ions and hydroxyl ions to form water. Total acidity is a measure of the total quantity of hydrogen ions which the solution is capable of furnishing when it is brought in contact with a base. A similar definition applies to total alkalinity. Total acidity is

most conveniently expressed in terms of normality, *i.e.*, moles of hydrogen ion per liter. Total acidity may also be expressed in terms of percentage of any acid which happens to be present. Total acidity or alkalinity is determined by titration with standard base or acid, respectively. The determination of total acidity by titration, using indicators, is described in the chapters dealing with the materials for which this determination is required. In colored or turbid solutions, in which the end point cannot well be found with indicators, an electrometric method may be used to determine the end point. This method is described at the close of this chapter.

Now, while the determination of total acidity tells the amount of hydrogen ion which the solution can furnish to neutralize a base, it tells nothing regarding the state of the hydrogen ions in the solution before the base is added. The acid may be highly dissociated, in which case most of the hydrogen ions will exist as such, or it may be very little dissociated, in which case most of the hydrogen ions will exist in combination with the anion as the undissociated acid, and the solution will contain very few free (or dissociated) hydrogen ions at any one time. For example, tenth-normal hydrochloric acid and tenth-normal acetic acid require exactly the same volume of tenth-normal sodium hydroxide per 100 cc. to render them neutral to phenolphthalein indicator, and hence the total acidity of their solutions is the same. But hydrochloric acid is almost completely dissociated into hydrogen and chloride ions, while acetic acid is dissociated only to the extent of about 1 per cent in tenth-normal solution. When alkali is added to the acetic acid solution, and these few hydrogen ions are used up by combining with hydroxyl ions, more of the acetic acid dissociates, and this process continues until all of the acid is neutralized by the base. But in the initial solutions, before any base is added, the concentration of dissociated hydrogen ions is roughly one hundred times as great in the tenth-normal hydrochloric acid as in the tenth-normal acetic acid. Thus, while the two solutions behave alike in reactions which depend upon the total quantity of substance *capable* of producing hydrogen ions (*total acidity*), they will behave very differently in respect to properties depending upon the number of hydrogen ions actually present in the dissociated state (*hydrogen-ion concentration*). For instance, tenth-normal hydrochloric acid has a sour taste (roughly) 100 times as strong

as that of tenth-normal acetic acid and dissolves zinc at a rate 100 times as fast as does the latter.

Hydrochloric acid is typical of strong acids (including also nitric and sulfuric) which are nearly completely dissociated. Acetic acid is typical of weak, or slightly dissociated, acids, which include boric, carbonic, and most organic acids. Similarly, there are strong, or highly dissociated, bases, including sodium, potassium, calcium, and barium hydroxides, while ammonia and many organic bases are typical of weak bases, which are only slightly dissociated. The hydrogen- and hydroxyl-ion concentration of solutions of many acids and bases have been tabulated by Thomas (41, 46).

Most of the effects of acids and bases which are important in the tannery are determined not by total acid concentration but rather by hydrogen-ion concentration, or "effective acidity," as it is sometimes called.

METHODS OF EXPRESSING HYDROGEN-ION CONCENTRATION

The simplest and most straightforward method of expressing hydrogen-ion concentration is in terms of normality, or moles per liter of hydrogen ion. This method, however, is inconvenient. The concentration of hydrogen ions in solutions of weak acids is very small. Tan liquors, which contain weak organic acids, usually have hydrogen-ion concentrations between ten-thousandth and one-millionth normal. These concentrations may be expressed either as clumsy figures, involving many ciphers, such as 0.000001*N* for millionth-normal, or else by the exponential notation $N = 1 \times 10^{-6}$, which is unfamiliar and confusing to men without formal scientific training. For this reason a special scale has been devised for expressing hydrogen-ion concentration, known as the "pH value" scale. The pH value of a solution is the negative logarithm of its hydrogen-ion concentration expressed in moles per liter. If the hydrogen-ion concentration is one-thousandth-normal, or $N = 1 \times 10^{-3}$, the logarithm to the base 10 of the hydrogen-ion concentration is -3 , and the negative logarithm or pH value is 3. Expressed mathematically,

$$\text{pH} = -\log_{10}[\text{H}^+]$$

where $[\text{H}^+]$ means concentration of hydrogen ions in moles per liter.¹

¹ In very concentrated solutions of acids, or solutions containing much sodium chloride, pH value, as determined by the hydrogen electrode, may

In pure water, the concentration of hydrogen ions is $1 \times 10^{-7}N$, and hence the pH value is 7. In pure water, the concentrations of hydrogen and hydroxyl ions are equal, and hence a pH value of 7 corresponds to true neutrality. In any solution, the concentration of hydrogen ions is inversely proportional to the concentration of hydroxyl ions; that is, the product of the concentrations of H^+ and OH^- is a constant. For this reason the concentration of hydroxyl ions in alkaline solutions can be obtained from the concentration of hydrogen ions, and this permits the use of the one pH scale for both alkaline and acid solutions. pH value smaller than 7 indicate acid solutions, and

TABLE 31.—RELATION BETWEEN pH VALUE, HYDROGEN-ION CONCENTRATION, AND HYDROXYL-ION CONCENTRATION

pH value	Concentration of hydrogen ion	Hydroxyl ion
0	$N \times 1.0$	$N \times 10^{-14}$
1	$N \times 0.1$	$N \times 10^{-13}$
2	$N \times 10^{-2}$	$N \times 10^{-12}$
3	$N \times 10^{-3}$	$N \times 10^{-11}$
4	$N \times 10^{-4}$	$N \times 10^{-10}$
5	$N \times 10^{-5}$	$N \times 10^{-9}$
6	$N \times 10^{-6}$	$N \times 10^{-8}$
7	$N \times 10^{-7}$	$N \times 10^{-7}$
8	$N \times 10^{-8}$	$N \times 10^{-6}$
9	$N \times 10^{-9}$	$N \times 10^{-5}$
10	$N \times 10^{-10}$	$N \times 10^{-4}$
11	$N \times 10^{-11}$	$N \times 10^{-3}$
12	$N \times 10^{-12}$	$N \times 10^{-2}$
13	$N \times 10^{-13}$	$N \times 0.1$
14	$N \times 10^{-14}$	$N \times 1.0$

the acidity *increases* as the pH value *diminishes*. pH values larger than 7 indicate alkaline solutions, and the alkalinity *increases* as the pH value *increases*. The pH values, hydrogen-

indicate a hydrogen-ion concentration greater than would be possible even if all the acid present were dissociated into hydrogen ions and anions. In such a case it is evident that the potentiometric method does not give the true concentration of hydrogen ions in terms of total volume of solution, although it may be giving it correctly in terms of uncombined water or of free space between the molecules. When we write $[H^+] = 1.5$, we do not mean that 1 l. of solution contains 1.5 moles of hydrogen ion but that the solution *acts* as though it contained 1.5 moles of hydrogen ion in 1 l. of ideal solution (46).

ion concentrations, and hydroxyl-ion concentrations of solutions ranging from normal acid to normal alkali are given in Table 31.

The hydrogen-ion concentration of solutions whose pH values are not whole numbers cannot be obtained from the pH values merely by pointing off the proper number of decimal places. The hydrogen-ion concentration of a solution of pH value 1.5 is not twentieth-normal but rather the number whose logarithm is -1.5 . In practice the occasion to translate pH values into hydrogen-ion concentrations seldom arises. Table 31 is given merely to assist those not familiar with the pH scale to correlate pH values with normality of acid or alkali.

Blackadder (5) suggested a linear scale for expressing hydrogen-ion concentration, in which the pH value of the isoelectric point of collagen (4.8) is taken as zero. Acidity values corresponding to pH values less than 4.8 are expressed by positive numbers, and those corresponding to pH values greater than 4.8 are expressed by negative numbers. The relation between pH values and Blackadder's acidity potentials is given below:

Acidity potential.....	4.0	3.0	2.0	1.0	0.0	-1.0
pH value.....	0.8	1.8	2.8	3.8	4.8	5.8
Acidity potential.....	-2.0	-3.0	-4.0	-5.0	-6.0	-7.0
pH value.....	6.8	7.8	8.8	9.8	10.8	11.8

The pH scale is sometimes known as the Sorenson scale, after its originator.

METHODS FOR MEASURING pH VALUE

There are two general methods in wide use for measuring pH value. The first, and more fundamental, of these is the potentiometric method. In this method, we measure the voltage of a cell consisting of two electrodes one of known potential and one whose potential varies as a function of the hydrogen-ion concentration and nothing else. Two such electrodes whose potential is strictly a function of hydrogen-ion concentration are the hydrogen electrode and the quinhydrone electrode. Either of these may be used, in combination with an electrode of known voltage, to measure pH value, and each possesses advantages over the other in special cases. The hydrogen electrode is the more generally useful for tannery liquors. The second general method is the indicator, or colorimetric, method, based on the fact that certain compounds assume definite shades depending upon the pH value. The indicator method has been greatly developed

during recent years and may now be used for almost every kind of solution. All colorimetric pH measurements are based, however, upon measurements made with the potentiometer, at least to determine the colors of indicators corresponding to different pH values and generally to prepare standards for comparison as well.

PRINCIPLE OF THE HYDROGEN ELECTRODE (46)

When a metal is dipped into a solution of one of its salts, an electrical potential difference is established between the metal and the solution due to differences in the tendencies for metal to pass into solution as ions and for ions to leave the solution and become deposited on the metal. The magnitude and sign of this potential difference are determined by the nature of the metal and the concentration of the ions of the metal in the solution. In the familiar Daniell cell, an electrode of copper is dipped into a solution of zinc sulfate. The zinc atoms have a great tendency to pass into solution as zinc ions, leaving their valence electrons on the zinc electrode, changing it negatively. The copper ions have a tendency to pass from the solution to the copper electrode, charging it positively. When contact is made between the two solutions, using a porous plate to prevent the zinc sulfate and copper sulfate solutions from mixing, the system becomes an electric cell with the zinc electrode the negative pole and the copper electrode the positive pole. The voltage of the cell is the difference of potential between the two electrodes. If the voltage of the cell and the potential at one of the electrodes are known, the potential at the other electrode can be calculated by difference.

If a cell is so constructed that the potential at one electrode is kept constant at a known value, then the voltage of the cell will vary as the potential of the other electrode. And, if the only variable factor operating at the second electrode is concentration of the active ion in the solution, the voltage of the cell will be a measure of this concentration. This principle is used in many kinds of measurements of ion concentration, including hydrogen-ion concentration.

In measuring hydrogen-ion concentration, the electrode of fixed potential is the so-called calomel electrode, consisting of mercury in contact with a solution saturated with mercurous chloride and containing potassium chloride. The latter may be

saturated, normal or tenth-normal, and the potential of the cell will vary by a constant amount depending upon the strength that is employed. The authors prefer the saturated potassium chloride-calomel electrode, for reasons stated later. The hydrogen electrode is a platinum wire whose surface is saturated with hydrogen gas, making it act toward the solution like an electrode of hydrogen, the platinum being practically inert. With increase of hydrogen-ion concentration in the solution, there is an increase in the tendency for hydrogen ions to pass from the solution to the electrode, increasing its positive electrical charge. Where hydrogen-ion concentration is the only variable, it can thus be measured by measuring the voltage of the cell as a whole. The method of obtaining hydrogen-ion concentration or pH value from the observed voltage is described later in the chapter.

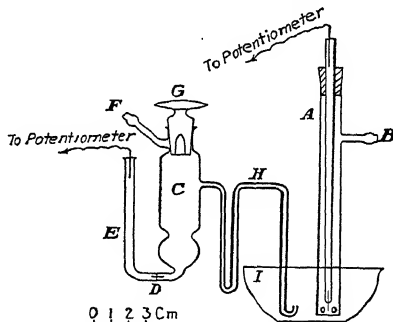


FIG. 47.—Hydrogen electrode vessels designed for use with tannery liquors.

HYDROGEN ELECTRODE VESSELS USED FOR TANNERY LIQUORS

Figure 47 shows a diagram of the electrode vessels developed from other forms by Wilson and Kern (47), to make them more suitable for use with tannery liquors. Batteries of these electrodes have been in daily use in the authors' laboratory for many years, for the testing of all kinds of tannery liquors, and have given very satisfactory results.

The outer portion of the hydrogen electrode vessel *A* is a straight glass tube with a side arm, the lower part being perforated with holes to assist in the escape of hydrogen. The purified hydrogen gas is passed in through side arm *B*. The electrode itself is a piece of 22-gage platinum wire from 1 to 2 cm. long, sealed in the end of a glass tube which passes through an

ordinary cork fitted to the outer tube. The electrode tube is filled with mercury, and contact with the potentiometer is made by inserting a wire from it into the open end of the electrode tube.

This simple form of hydrogen electrode offers many advantages over the more elaborate forms sometimes employed. The electrodes are so cheap that a large number can be made up and kept on hand. Whenever there is the slightest suspicion that the electrode has become poisoned, the suspected electrode can be removed and a fresh one inserted almost instantaneously. The used electrodes are easily cleaned by dipping them for a few seconds into hot aqua regia. The use of a wire electrode of small exposed area helps to bring the system to equilibrium more rapidly, which is desirable in titrating and in working with liquors that poison the electrode easily.

Vessel *C* is the calomel cell. At point *D* the tube is sealed off with a platinum wire making contact between the separated portions. The side arm *E* is used for making contact with the potentiometer; it is filled with mercury and a lead wire introduced into the open end. The bulb of the cell is filled with mercury covered with a layer of mercury-mercurous chloride paste, and the cell is kept filled with a saturated solution of potassium chloride and mercurous chloride, which enters the cell from a large reservoir through the side arm *F*, the flow being regulated by the stopcock *G*. Before and after using the cell, the cell is flushed by opening *G*. The overflow passes out through the capillary side arm *H*. The solution whose potential is to be measured is placed in dish *I*.

The deep *U* in the capillary tube prevents contamination of the calomel cell by the tannery liquor, which usually has a lower specific gravity than the solution in the cell. One of these electrodes may be used for months without any cleaning beyond flushing out before and after each measurement.

PLATINIZING THE ELECTRODES

The platinum wire constituting the hydrogen electrode must be covered with a thin coating of platinum black, deposited electrolytically. After the electrode has been used from one to half a dozen times, it generally becomes poisoned, when the old coating must be removed and a new one deposited. The authors have found the following procedure to work well:

Thoroughly clean the electrode by dipping it into a hot mixture of 3 parts of concentrated hydrochloric and 1 part concentrated nitric acid. Leave the electrode in the solution until the metal is clean and bright. Do not leave the electrode in the aqua regia longer than necessary, to avoid loss of platinum. Then rinse the electrode first in running tap water, then in distilled water, and suspend it in distilled water until ready to platinize. An ordinary test tube with a cork pierced with a hole wide enough to admit the electrode easily makes a convenient holder. An alternate method of cleaning the electrodes is by electrolysis (26). The electrode is connected to the positive pole of a battery of two dry cells, and a dummy electrode is connected to the negative pole. Both electrodes are dipped into concentrated hydrochloric acid. The chlorine liberated at the positive pole rapidly removes the coating of platinum black. In order to shorten the time required for cleaning, electrodes heavily coated with organic matter should be dipped first into hot chromic acid solution for a few minutes, then rinsed, and platinum dissolved as described above.

It is absolutely necessary that the electrodes be thoroughly clean before platinizing. Under no other conditions can a satisfactory deposit of platinum be obtained. If the electrolytic method for cleaning is used, the electrode can be considered clean when the gas comes off in numerous very small bubbles; the evolution of a few large bubbles indicates that cleaning is incomplete.

To deposit platinum, the authors recommend the use of a 3-per cent solution of platinic chloride in half-normal hydrochloric acid. Many authorities (26) advise the addition of 0.025 per cent lead acetate to the platinic chloride. The electrode to be platinized is connected to the negative pole of a 4-volt battery, and the positive pole is connected to a dummy electrode. Both electrodes are dipped into the platinizing solution. This is conveniently kept in a small glass-stoppered weighing bottle; 25 cc. of the solution will last a long time. The current is allowed to pass until a uniform, jet-black coating of platinum is deposited on the electrode. The time required to produce this coating varies with the strength of the solution (which of course becomes exhausted as it is used), the amount of current furnished by the battery, the distance the electrodes are apart, etc. The appearance of the proper coating can be learned only by experience, but it may be said that it is essential that the entire exposed surface of the wire be coated with a jet-black deposit and that the electrolysis should not be prolonged until the electrode assumes a fuzzy appearance. Underplatinized electrodes poison easily, while overplatinized electrodes are too slow in coming to equilibrium. With a fresh solution and a freshly

charged battery, 30 sec. platinization is about right. This time may rise to as long as 5 min. as the solution or the source of current becomes depleted.

During platinization gas should be evolved in minute bubbles from all parts of the electrode surface; the formation of larger bubbles that cling to the electrode indicates that the surface was not properly cleaned.

After platinization, the electrode is charged with hydrogen by connecting it to the negative pole of a 4-volt battery, connecting a dummy electrode to the positive pole, and suspending both electrodes in a 10-per cent solution of sulfuric acid for a few minutes. The electrode is then ready for use. Suspend it in a test tube of distilled water until it is needed; never allow any electrode to dry out.

PREPARING THE CALOMEL ELECTRODE

The calomel electrode vessel (*C*, Fig. 47) must first be thoroughly cleaned with a hot chromic acid solution, then rinsed with distilled water. Then place about 15 g. of highly purified mercury¹ in the vessel so that the platinum lead wire *D* is covered. Then mix about 5 g. of pure mercury and 5 g. of specially purified calomel by grinding in an agate mortar with a little saturated potassium chloride solution, and put in enough of the mixture to form a layer over the mercury. Fill the vessel nearly full with a solution saturated with potassium chloride and specially purified mercurous chloride. Connect the side arm *F* (Fig. 47) with a reservoir containing about 2 l. of this solution and an excess of the crystals of both salts, open *G*, and let the solution run through the electrode until the capillary side arm *H* is full. Keep the tip of the capillary under water at all times.

In place of saturated potassium chloride, some workers use either a tenth-normal or a normal solution. If either of these is used, the relation between pH value and voltage will be different from that given in this chapter. In using potentiometers reading directly in pH units, such as the portable acidity meter described below, it is necessary to specify what strength of potassium chloride is to be used when ordering the instrument. When the concentration of potassium chloride is large, slight

¹ Mercury, and other materials, specially purified for use in pH measurements may be bought from dealers specializing in apparatus for hydrogen-ion control, such as Leeds and Northrup Company and Lamotte Chemical Products Co.

differences in concentration, that may occur because of diffusion or changes in solubility of the potassium chloride with temperature, have very little effect on the potential of the electrode, while when the concentration is low (*e.g.*, tenth-normal), small

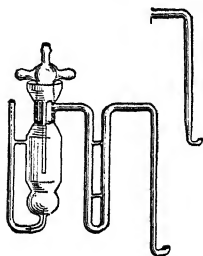


FIG. 48.—Calomel electrode vessel with mercury seal.

changes in concentration have a very marked effect on the potential. The saturated potassium chloride-calomel electrode has a lower temperature coefficient (16) than calomel electrodes containing potassium chloride of other strengths, and by means of the excess of solid salt in the reservoir the concentration is maintained constant at all times. Saturated potassium chloride solution has a notable tendency toward "creeping." This can be minimized by keeping the connections well greased. The Leeds and Northrup

Company (26) has designed a modified form of the calomel electrode vessel, shown in Fig. 48, which has a mercury seal to prevent creeping of the solution about the stopcock.

HYDROGEN SUPPLY

By far the cheapest and most convenient method of supplying hydrogen is from cylinders. The 100-ft. size is most suitable for a laboratory installation; smaller sizes may be obtained if the whole outfit must be moved from place to place. The hydrogen cylinder must be equipped with a pressure-reducing valve.¹

The hydrogen must be purified by passing through a purification train. The system used by the authors consists of (1) a saturated solution of mercuric chloride, (2) a nearly saturated solution of potassium permanganate made alkaline with sodium hydroxide, (3) a strong solution of pyrogallol made alkaline with sodium hydroxide, and (4) a spray trap consisting of a tower packed with glass wool or cotton. The solutions are used in ordinary Drechsel wash bottles. The outlet of the spray trap is connected to side arm B (Fig. 47). When the permanganate solution becomes green instead of violet, all the solutions should be renewed at once.

¹Sold by Leeds and Northrup Company or by dealers in cutting and welding equipment.

ASSEMBLY OF APPARATUS

The complete equipment used for determining pH values in the authors' laboratory is shown in Fig. 49 (at the left) (46). The hydrogen tank is under the table. The gas passes through a rubber tube to the 3 Drechsel bottles and spray trap on the elevated shelf. From the spray trap the gas passes by a system of *T*'s and stopcocks to the eight hydrogen electrodes. Each hydrogen electrode is held by a clamp attached to a ring stand. The potassium chloride-calomel solution is kept in the aspirator bottle at the extreme left end of the shelf and is distributed to the



FIG. 49.—Assembled apparatus for determining pH value.

8 calomel electrodes by *T*'s and stopcocks. The calomel electrodes are clamped to the stands carrying the hydrogen electrodes. The solutions to be tested are placed in 100-cc. lipped Pyrex glass dishes. Each dish is supported on a glass plate resting on a 6-in. iron ring clamped to the ring stand. To change the solution under any pair of electrodes, it is necessary only to lift the dish slightly with one hand, slip out the glass plate with the other, lower the dish to the desk through the ring, and bring the dish containing the new solution into position in the same way.

The lead wires from each pair of electrodes are connected to the center binding posts of one of the double-throw switches

shown. The upper terminals of these switches are connected to a recording potentiometer (against the wall); the lower terminals are connected to the type K potentiometer at the front of the work bench. This potentiometer operates from a single storage cell, placed under the table, connection being made by the lead wires extending over the front edge of the table.

It is not necessary to have so many as 8 sets of hydrogen and calomel electrodes set up and in use at once, although this number is very convenient if series of determinations are to be run, but at least 2 hydrogen and calomel electrodes should be in readiness for use at all times, with preferably a third calomel electrode made up as a replacement. At least a dozen hydrogen electrodes should be kept on hand, platinized and ready for use.

PRINCIPLE OF THE POTENTIOMETER

The potentiometer is an instrument for measuring the potential, or voltage, of a cell. In determining pH values, the cell to be

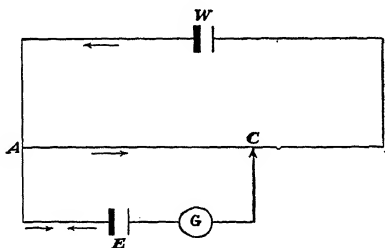


FIG. 50.—Principle of the potentiometer.

measured consists of a combination of an electrode of known potential, usually the calomel electrode, and one of unknown potential whose voltage is a function of the hydrogen-ion concentration. The latter may be either the quinhydrone or the hydrogen electrode. To measure the voltage of such a cell, the cell is introduced into a circuit in such a manner that its potential is opposed to a known potential, which can be varied. When the potential of the cell exactly balances that of the working cell, no current passes through the circuit. This condition is ascertained by testing the circuit with a galvanometer, which is not deflected when the potentials are exactly balanced.

The method of balancing the potential of the unknown cell against the known potential is, in principle, as follows (26):

The terminals of a standard cell of known voltage are connected by means of wires of negligible resistance to the ends of a resistance wire of uniform cross-section. The resistance of such a wire is proportional to its length. The total fall of potential along this wire is equal to the voltage of the standard cell, and the fall of potential along any section of the wire is to the total fall as the length, *i.e.*, the resistance, of that section is to the total length (total resistance) of the wire. Thus, in Fig. 50, the difference of potential between *A* and *C* is to the total difference of potential between *A* and *B* (which is equal to the potential of the cell *W*) as the length *AC* is to the length *AB*. Now, if the cell whose voltage is to be measured (*E*) is introduced into the circuit between *A* and *C*, in such a manner that its potential opposes that of *W*, the distance *AC* can be varied by moving the contact *C* until the fall of potential between *A* and *C* is exactly equal in magnitude and opposite in sign to the voltage of the cell *E*. When this condition is attained, no current can pass between *A* and *C*, and the galvanometer *G* will show no deflection. The voltage of *E* can then be found from the proportion

$$E:W::AC:AB$$

The essential parts of a potentiometer are, then, a standard cell of known and constant e.m.f., a resistance wire whose resistance is a function of its length, and a galvanometer. In practical potentiometers, the arrangement of these essential parts is somewhat different from that shown in Fig. 50. The actual arrangement commonly used is shown in Fig. 51 (26). Instead of using the standard cell in making the measurement, current is drawn from an ordinary storage cell or dry cell *W*. The current drawn from this cell is regulated by the rheostat *R*. The resistance wire *AB* is not a single straight wire, which would have to be excessively long to obtain precision, but is composed of a number of resistance coils, all alike, connected in series, and a slide wire equal in resistance to one of the resistance coils. The cell whose potential is to be measured (*EMF*) makes contact with this series of resistances at two movable points *M* and *M'* instead of at one fixed and one movable point, as shown in Fig. 50. By moving *M*, any whole number of the resistance coils is brought into play, and by moving *M'* any required portion of the slide wire is added to the resistance coils. The resistance between

M and M' therefore corresponds to the resistance AC of Fig. 50. In the type of potentiometer whose use is described in this chapter, the resistance coils are so constructed that the fall of potential is 0.1 volt for each coil when a current of 0.02 amp. flows through the circuit. Thus if there are 15 coils, the total fall of potential through all the resistance coils is 1.5 volts. The slide wire is so constructed that 100 units on its scale corresponds to another 0.1 volts, making the total difference of potential between A and B 1.6 volts. (Actually the scale of the slide wire extends to 110 units, corresponding to 0.110 volt, so that the total potential difference is 1.610 volt. This construction makes the slide wire overlap each of the resistance coils.) Thus if the points M and M' are so set that the resistance between them comprises five

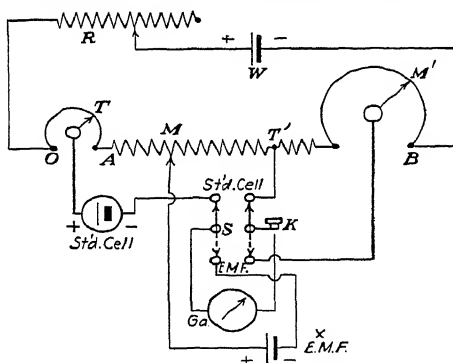


FIG. 51.—Usual arrangement of potentiometer circuit.

resistance coils and 60 units of the slide wire when the potential of the unknown cell is balanced against the working current, then the voltage of the unknown cell is $(0.1 \times 5) + 0.060$ volts, or 0.560 volts. To regulate the current provided by the working cell W so that it shall always be 0.02 amp., the working cell is balanced against the standard cell. The voltage of the standard cadmium cell is about 1.0166 volts, varying slightly with different individual cells. As shown in Fig. 51, the standard cell is shunted across a portion of the resistance AB . The contact with the resistance coils (T') is fixed; the second contact T is made by a movable slider on the resistance wire OA . This contact is set once for all so that the resistance TT' corresponds to a potential drop of 1.0166 volts, or whatever the voltage of the standard cell may be. (The standard cells are calibrated by the manu-

facturer, and the actual voltage of each particular cell is certified.) By means of the double-throw switch S , the standard cell is thrown into the circuit with its e.m.f. opposing that of the working current through the resistance TT' . If the working current is exactly 0.02 amp., the standard cell will exactly balance the working cell, and no current will flow through the galvanometer.



FIG. 52.—General view of the portable acidity meter (Leeds and Northrup Company).

If the working current is not exactly 0.02 amp., it is made so by varying the resistance R . This arrangement is necessary because the voltage of the standard cell would not long remain constant if current were drawn from it in making the actual measurements. By using the standard cell only to adjust the working current, the standard cell is called upon only to deliver

a minute current at infrequent intervals and so maintains a constant voltage indefinitely.

A tapping key *K* is introduced into the circuit so that no current flows through the galvanometer except when the key is depressed. In making a measurement, the resistances are adjusted to approximately the values required to produce a balance between the unknown potential and the working current, then the key is tapped, and the direction of deflection of the galvanometer is noted. The resistance is then increased or decreased, as required, until the galvanometer shows no deflection on tapping the key.

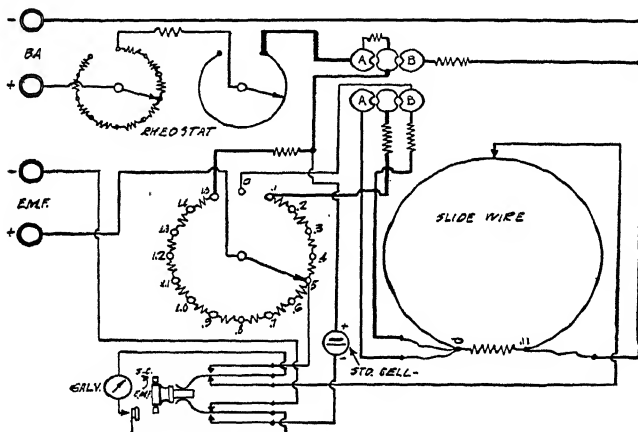


FIG. 53.—Construction of the portable acidity meter.

The sensitivity of a potentiometer is determined by the sensitivity of the galvanometer employed. The accuracy of a potentiometer depends upon the accuracy of construction of its resistance coils and slide wire.

CONSTRUCTION AND OPERATION OF POTENTIOMETERS

Of the numerous types of potentiometer on the market, the authors have used, and found satisfactory, the Leeds and Northrup portable acidity meter (26). A general view of this instrument is given in Fig. 52, and its construction is shown diagrammatically in Fig. 53. The acidity meter has all the essential working parts (except electrodes), including standard

cell, working cell, resistances, and galvanometer, contained in a substantial oak case, that can be transported easily from one department to another. The resistances and contacts are all inside the box, under a Bakelite cover, and hence are protected from dust and corrosion. The precision of the instrument is better than 0.5 mv., or about 0.01 pH unit, which is ample for all control and most research work, when measurements are made at 25°C. Even if the temperature varies from 20 to 30°C., the precision is better than 0.05 pH unit, which is ample for most control work. The instrument is equipped with two scales, one reading in volts, and the other in pH or Blackadder units. The galvanometer is very rugged and not easily gotten out of order. Current is provided by dry cells, contained in the case, or, if desired, by storage cells, for the connection of which binding posts are provided. When the instrument is used in the laboratory, storage cells possess some advantages, as the small dry cells used have a comparatively short life.

In operating the acidity meter, the hydrogen and calomel electrodes are connected to the binding posts marked *E.M.F.* at the left of the top plate of the instrument. The polarities of these posts are indicated. Connect the calomel electrode to the positive and the hydrogen electrode to the negative *E.M.F.* post.

Adjustment of the working current is accomplished by two rheostats, controlled by dials located in the upper left portion of the top plate (Fig. 52). The left dial is for coarse and the right dial for fine adjustment. In regulating the current, the plugs shown at the upper right of the top plate must be placed in the holes marked *A*. Set the coarse adjusting dial at 9, and turn the fine adjusting dial as far as possible in the clockwise direction. Turn the rotating switch at the lower right center of the top plate so that the arrow points to the points to the letters *S.C.* (standard cell). Tap the key *GA.* (galvanometer), shown at the lower left center of the top plate, with a short, quick tap, and note the direction of deflection of the galvanometer needle. Then turn the coarse adjusting dial so as to decrease the deflection, tapping the *GA.* key after each adjustment of the dial. When the point is reached at which the galvanometer deflection is in the direction opposite to that which it had originally, start turning the fine-adjusting rheostat in the counterclockwise direction, and tap the key at intervals until a position is found at which the galvanometer shows no deflection. The current in the potentiometer

is then adjusted in accordance with the standard cell, and measurements may be made.

The current through the potentiometer may alter slightly at times, so that occasionally the current should be checked, and slightly readjusted if necessary by moving the fine adjustment rheostat. When such checking or readjustment is to be done, the two plugs must be in the position marked *A*, and the rotating switch at the lower right center of the top plate must be in the position marked *S.C.* When the coarse adjustment rheostat has been turned to zero, and the fine adjustment rheostat has been turned in a counterclockwise direction as far as possible in order to establish a balance, it is necessary to replace the dry cells in the compartment at the right end of the instrument or, if an external storage battery is being used, to recharge the battery.

In making measurements, the rotating switch at the lower right center is turned to the position marked *E.M.F.* If the reading is desired in volts, the two plugs at the upper right are left in the holes marked *A*. If the reading is desired in pH units, the plugs are moved to the holes marked *B*. The plugs must be returned to *A* when checking the potentiometer current. Then the knob at the lower right of the top plate, which controls the contact on the slide wire, is turned so that the scale (viewed through the peep hole just below the knob), reads 0.1. The main dial on the left, which controls the contact with the resistance coils, is set at zero. The *GA.* key is tapped, the direction of deflection noted, and then the main dial is rotated in the direction to increase the voltage or pH reading, the galvanometer key being tapped quickly at each step. When the direction of deflection of the galvanometer needles reverses, the main dial is left in the position it then occupies, and the slide-wire dial is turned so as to decrease the reading, until the galvanometer shows no deflection.

The voltage, or pH value, depending upon the scale employed, is read directly from the position of the two dials. The main (left) dial reads directly in tenths of a volt, or whole pH units. The slide-wire dial (right) reads directly in thousandths of a volt (tenths and hundredths of a pH unit), and by interpolation the reading can be carried one decimal place farther. Suppose, using the volt scale, the main dial is set at 1.2 and the cross-hair over the slide-wire scale is between six and seven small divisions to the right of the figure 0.03 on the slide-wire voltage scale.

The reading of the slide-wire dial is then between 0.036 and 0.037, and upon estimating the fraction of the smallest scale unit we may decide that the reading is 0.0367. The voltage, then, is $1.2 + 0.0367$ or 1.2367 volts. If the pH scale has been employed, the same setting of the dial would indicate 12.367 pH units.

RECORDING POTENTIOMETER (26)

This instrument works on the same principle as the one described above but is provided with a mechanism by means of

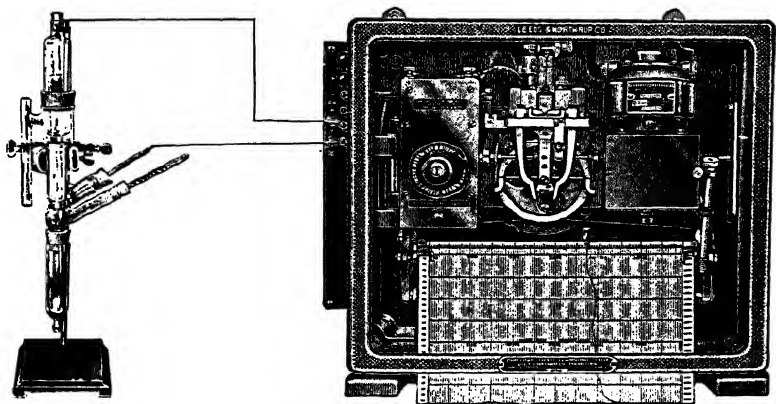


FIG. 54.—Recording potentiometer (Leeds and Northrup Company), connected to continuous flow hydrogen and calomel electrodes for determining pH value continuously.

which the slide-wire contact is shifted automatically until the position is reached at which no deflection of the galvanometer occurs. When the galvanometer swings, the needle interrupts the motion of a series of motor-driven levers, causing them to turn the slide wire of the potentiometer. A pen moves with the slide wire and traces a line on a motor-driven chart. A signaling device causes a buzzer to sound when the pH value passes any designated value.

The recording potentiometer is useful in determining the pH value of industrial liquors continuously, for which purpose it must be used with special types of calomel and hydrogen electrodes (26). It is also useful in titrations and in determining the pH values of liquors in which equilibrium at the electrodes is established slowly. In such liquors, the machine is started,

and the chart examined occasionally until the line traced has become vertical, showing that the voltage of balance has become constant.

A recording potentiometer is shown in Fig. 54.

CARRYING OUT A DETERMINATION OF pH

Clean a dozen or more hydrogen electrodes and platinize them as described under Platinizing the Electrodes. Flush each calomel electrode by opening the stopcocks momentarily and allowing a little potassium chloride solution to flow through the capillary. Inspect each calomel electrode to see that there are no air bubbles in the capillaries. Place a dish containing about 50 cc. of distilled water under each electrode. Place platinized hydrogen electrodes in two or more of the outer glass tubes *A* (Fig. 47), and close the unused hydrogen electrode tubes with corks. Adjust the position of the hydrogen electrodes by sliding the electrode up or down through its cork until the platinum wire is about half immersed in the water. Open the stopcocks on the hydrogen supply lines leading to the electrodes to be used. Close the pressure-reducing valve on the hydrogen tank, and open the main valve of the tank. Very cautiously open the pressure-reducing valve, until hydrogen begins to pass through the purification train in a steady stream. Adjust the flow of hydrogen at each electrode, either by manipulating the stopcocks in the individual feed lines or, better, by raising and lowering the hydrogen electrode vessel with reference to the level of the liquid in the dish, until the gas escapes from each electrode at a rate of about one bubble per second. The tip of the electrode should just touch the liquid when the liquid is depressed to the fullest extent by the gas pressure. Allow the gas to pass over the hydrogen electrodes in distilled water for a few minutes to ensure saturation of the electrodes with gas and to displace all air from the system.

Connect the hydrogen and calomel electrodes to the switches by inserting the lead wires in the mercury contact tubes. See that contact is made with the mercury in every case. Open all the switches.

Adjust the current in the potentiometer as described above.

Test the electrodes, one by one, by closing each switch in turn to connect each cell to the potentiometer and determining the voltage (or pH) of the hydrogen electrode-calomel electrode combination in water. To determine the voltage of each combination, insert the plugs shown at the top of the instrument in Fig. 52 in the *A* holes. Turn the rotating switch so that the arrow points to *E.M.F.* Set the main resistance dial on 0.0 volts, and set the slide-wire dial so that the scale reads 0.1 volt. Tap the *GA.* key, note the direction of deflection of the galvanometer, and turn the main dial so as to increase the reading by steps of 0.1 volt, tapping the key at each step, until the direction of deflection reverses. Then turn the slide-wire dial to decrease the slide-scale reading by steps of 0.01 volt, tapping the key at each step, until a second reversal of the direction of deflection is obtained, then increase the reading by steps of 0.001 volt, and so on until no deflection of the galvanometer takes place when the key is tapped. Record the reading. Similarly, obtain a balance with each pair of hydrogen and calomel elec-

trodes. Then return to the first pair tested, and obtain a balance again, to see if the voltage of the combination is constant. The voltage of each pair, in distilled water, should quickly come to equilibrium and should read about 0.5 volt. If the pH scale is used, the reading should be in the neighborhood of 5 pH units. The reading should not fluctuate; a falling voltage indicates a poisoned electrode, while a very slowly rising voltage probably means overplatinization.

As soon as the electrode gives a constant reading in water, place 50 cc. of the solution to be tested in a dish and place the dish under one pair of electrodes. Obtain the setting of the instrument for zero deflection as described above. Wait about 2 min., and check the reading. Continue until the reading does not change by more than 0.5 mv. in 2 min. Take the temperature of the solution in degrees centigrade. Then place the solution under a second hydrogen electrode-calomel electrode combination and obtain a balance as before. The two readings should agree.

If the reading obtained with any hydrogen electrode shows a steady falling off with time, the electrode should be rejected and a fresh one inserted. For this reason it is well to have several electrodes set up in distilled water with hydrogen bubbling over them at all times, so as to be instantly available.

In the case of solutions known to have a tendency to poison the electrodes, it is well to saturate the solution with hydrogen before inserting the electrode, as a quicker equilibrium balance is thereby obtained. To saturate the solution, place the dish containing it under one of the empty, corked, hydrogen electrode tubes, and pass the gas through the solution for about 10 min.

After each determination, the hydrogen electrode should be rinsed and then brought to equilibrium with distilled water and its voltage ascertained. If the voltage comes rapidly to equilibrium at a value of about 0.5 volt, the electrode may be used over again, otherwise it should be set aside for cleaning and replatinization.

The calomel electrode should be flushed after each determination.

CALCULATION OF pH FROM VOLTAGE

If the portable acidity meter is used, pH values may be obtained directly, if the plugs are placed in the *B* holes. If the balance is obtained with the plugs in the *A* holes, or if an instrument is used that does not have a pH scale, the voltage must be transposed to pH units. This is done from the equation

$$\text{pH value} = \frac{V - 0.2450}{0.0001983T}$$

where *V* is the observed voltage of the hydrogen electrode-calomel electrode combination in the solution in question, 0.2450 is the voltage of the *saturated* potassium chloride-calomel electrode, and *T* is the *absolute* temperature (degrees centigrade plus 273). If the normal or tenth-normal potassium chloride-

calomel electrode is used, the values of the constant in the numerator must be increased by 0.0380 and 0.0910, respectively.¹ If the temperature at which the determination is carried out is far removed from 25°C., the constant 0.2450 must be increased by 0.0002 volt for each degree rise above 25° and decreased by 0.0002 for each degree fall below 25°C. Fales and Mudge (16) found the temperature coefficient of the calomel half cell to be 0.0002 volt per degree between 5 and 60°C.

The equation given is strictly valid only when the hydrogen is at a pressure of 760 mm. In actual measurements the hydrogen

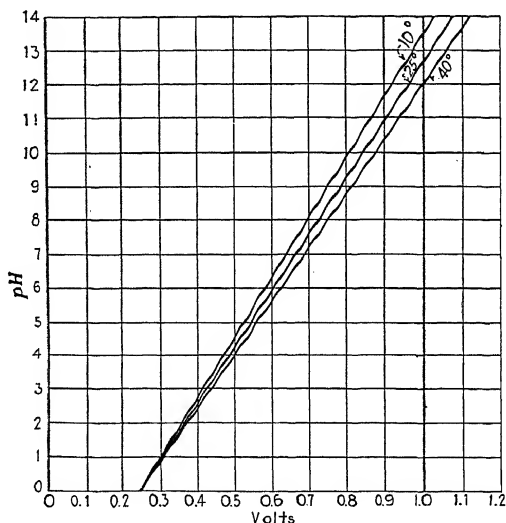


Fig. 55.—Relation between e.m.f. and pH value at different temperatures.

is at the prevailing atmospheric pressure, minus the vapor pressure of the solution at the temperature employed, and plus the very small back pressure exerted by the liquid in the dish. For ordinary purposes, these factors may be ignored. Tables for correcting the readings obtained to 760 mm. pressure are given by Clark (11).

¹ The value 0.2450 is that found by Fales and Mudge. Other authorities give slightly different values, *e.g.*, 0.2458 (Clark) and 0.2464 (Leeds and Northrup). So long as one fixed value is used for all determinations, the differences are of no practical importance.

Instead of calculating the results of each determination from the equation, it is advisable to construct charts by means of which the pH value corresponding to any voltage at any temperature can be read off at a glance. At any temperature, pH value is a linear function of voltage, therefore it is only necessary to calculate the pH values corresponding to 2 arbitrarily selected voltages at one temperature, plot voltage as abscissa and pH value as ordinate, and connect the points by a straight line. pH values corresponding to any voltage, determined at this tem-

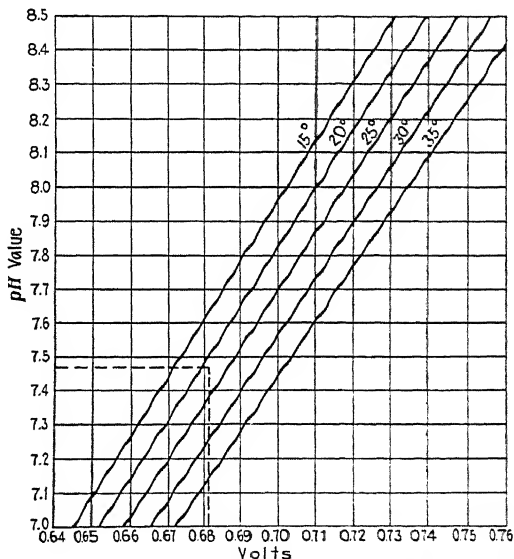


FIG. 56.—Working chart for finding pH from measured voltage.

perature, can be obtained from this graph. Similar graphs are thus constructed for temperatures 5° apart over the working range. When the temperature of the determination is between two of the temperatures for which graphs have been constructed, the pH value corresponding to the determined voltage at that temperature is found by interpolation.

A small-scale chart of this sort, covering the whole pH range from 0 to 14, with graphs for temperatures of 10, 25, and $40^{\circ}\text{C}.$, is given in Fig. 55. For actual work, a set of larger-scale charts should be constructed, each single chart covering a range of

about 0.1 volt, with graphs for temperatures 5° apart. A sample chart of this kind, covering the pH range 7.0 to 8.6, is given in Fig. 56. Squared paper measuring 6 by 9 in., with 20 lines to the inch, was used in making this chart, but in the figure only every tenth line is shown, for the sake of clarity. To find the pH value corresponding to the experimentally determined voltage 0.6820 volt, when the temperature is 22°, find the point on the horizontal scale corresponding to 0.682, and measure upward along the vertical line intersecting this point to a point three-fifths of the vertical distance from the 25° line to the 20° line, as shown by the dotted lines in Fig. 56. Then carry a line horizontally from this point to the vertical scale, and read the pH value from the vertical scale. The pH value of the solution giving a voltage of 0.6820 volt, measured at 22°C., is thus found to be 7.47.

TABLE 32.—RELATION BETWEEN E.M.F. AND pH VALUE AT DIFFERENT TEMPERATURES

Calculated from equation

$$\text{pH value} = \frac{V - 0.2450}{0.0001983T}$$

where V is the e.m.f. of the hydrogen electrode-saturated calomel electrode combination, 0.2450 is the e.m.f. of the saturated calomel electrode, and T is the absolute temperature (centigrade temperature plus 273)

pH value	E.m.f. of hydrogen electrode-calomel electrode combination at the temperature indicated				
	15°	20°	25°	30°	35°
0	0.2450	0.2450	0.2450	0.2450	0.2450
1	0.3021	0.3031	0.3041	0.3051	0.3061
2	0.3592	0.3612	0.3632	0.3652	0.3671
3	0.4163	0.4193	0.4223	0.4253	0.4282
4	0.4734	0.4774	0.4814	0.4854	0.4893
5	0.5305	0.5355	0.5404	0.5454	0.5503
6	0.5877	0.5936	0.5995	0.6055	0.6114
7	0.6448	0.6517	0.6586	0.6656	0.6725
8	0.7019	0.7098	0.7177	0.7257	0.7336
9	0.7590	0.7679	0.7768	0.7858	0.7946
10	0.8161	0.8260	0.8359	0.8458	0.8557
11	0.8732	0.8841	0.8950	0.9059	0.9168
12	0.9303	0.9422	0.9540	0.9659	0.9778
13	0.9874	1.0003	1.0131	1.0260	1.0389
14	1.0445	1.0584	1.0722	1.0861	1.1000

Values from which such a set of charts may be constructed are given in Table 32.

STANDARDIZING pH MEASUREMENTS

To make certain that all parts of the set-up, particularly the hydrogen and calomel electrodes, are in proper condition and that the pH values obtained are the correct ones, it is necessary to determine the pH value of a solution of known hydrogen-ion concentration. The solution recommended by Clark (11) for routine checking of measurements is twentieth-molar potassium hydrogen phthalate. The pH value of this solution is 3.97 at 20°C. The potassium hydrogen phthalate used must be specially prepared for the purpose. Directions for preparing the salt are given by Clark, or material already purified may be purchased from firms specializing in apparatus for the determination of pH value. The twentieth-molar solution is prepared by dissolving exactly 5.1045 g. of the salt in water and making up to exactly 500 cc. The advantages of potassium hydrogen phthalate as a standard are that the salt may be obtained very pure by recrystallization, that it contains no water of crystallization, is not hygroscopic, and is an excellent buffer; that is, the pH value of its solution changes very little on slight dilution or concentration or upon the addition of small quantities of acid or alkali.

The Leeds and Northrup Company recommend and sell an acetate buffer solution giving a pH value of 4.63 at 25°C.

SPECIAL CASES: SOURCES OF TROUBLE

There are some solutions in which the hydrogen electrode cannot be used for determining hydrogen-ion concentration. In any solution containing an easily oxidizable or reducible ion, an oxidation-reduction potential is set up which masks the potential due to hydrogen ions. Such a case is a solution containing iron salts. Poisoning of the electrode has already been mentioned. Two ions having a pronounced poisoning action that are often encountered in tannery solutions are the sulfite and the sulfide ion. Pleass (34) showed that in tan liquors containing as little as 0.0003 per cent sodium sulfide, or 0.05 per cent sodium sulfite, the observed pH values are lower than the true ones; in lime liquors 0.1 per cent sodium sulfide causes the reading to be too low. For such solutions, the colorimetric method may sometimes

be used (but sulfides produce abnormal shades with many indicators). If only approximate results are required, they may sometimes be obtained by thoroughly saturating both the electrode and the solution with hydrogen, introducing the electrode into the solution, and obtaining a balance as rapidly as possible. The first reading obtained is recorded, without waiting to see whether or not equilibrium has been established. This procedure is repeated three or four times, using a fresh electrode each time, and the highest value so obtained is accepted as approximately correct.

The following suggestions, some of which may appear very obvious, may prove helpful to the beginner.

1. If no deflection of the galvanometer takes place when the key is tapped the first time in making a measurement, there is probably a loose connection somewhere or possibly an air bubble in the capillary side arm of the calomel electrode.

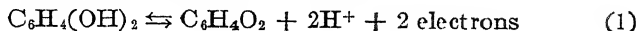
2. If the potentiometer seems very insensitive, that is, if the galvanometer is only slightly deflected even when the main potentiometer dial is turned through 0.1 or 0.2 volt, the resistance of the system is too high. This may be due to the solution under examination being a poor conductor, in which case the trouble can be remedied by emitting a few drops of saturated potassium chloride solution from the calomel electrode; if this fails to help, examine all connections, especially at switches and binding posts, cleaning the metal parts at the contact points. With the portable type of potentiometer, there is rarely any trouble due to poor contact between the wire and the slider; with other types having the slide wire exposed, the wire should be cleaned by rubbing vigorously with a soft cloth dipped in vaseline.

3. If the hydrogen electrodes fail to come promptly to a voltage of about 0.5 in distilled water, the trouble may be due to improper platinization or to impurities in the gas, due to exhaustion of the purification train solutions or of some of them.

4. If the electrodes show the normal voltage with water or with one of the standards mentioned above, but the voltage falls off rapidly to zero when the electrode is placed in the liquor, the probability is that the solution contains something which is poisoning the electrode. If this happens repeatedly with successive electrodes, carefully platinized, it is probable that no accurate measurement of the pH value of the solution can be made with the hydrogen electrode.

THE QUINHYDRONE ELECTRODE

When benzoquinhydrone, commonly known as quinhydrone, is dissolved in water, it is highly dissociated into equimolecular parts of quinone and hydroquinone (18), which are in equilibrium with each other according to the equation



If a platinum or, better, a gold wire is dipped into such a solution, a potential difference is set up between the solution and the wire. The voltage of such an electrode depends upon the relative amounts of quinone, hydroquinone, and hydrogen ion present in the solution. From Peter's form of the Van't Hoff isotherm, we have

$$0.000198T \log \frac{[\text{C}_6\text{H}_4\text{O}_2]}{[\text{C}_6\text{H}_4(\text{OH})_2]} = 0.000198T \log [\text{H}^+] \quad (2)$$

where π_m is the measured electrode potential and π_0 is the potential when the activity of all components of the system is normal. Now when the concentrations of quinone and hydroquinone are the same, which is the case when benzoquinone is dissolved, unless some oxidizing or reducing agent is present, then the expression

$$\log \frac{[\text{C}_6\text{H}_4\text{O}_2]}{[\text{C}_6\text{H}_4(\text{OH})_2]}$$

equals zero, and the equation becomes

$$-\log [\text{H}^+] = \frac{\pi_0 - \pi_m}{0.000198T} \quad (3)$$

But $-\log [\text{H}^+] = \text{pH}$ value, and so the equation can be written

$$\text{pH} = \frac{\pi_0 - \pi_m}{0.000198T} \quad (4)$$

π_0 was found by Büllmann (3,4), and by LaMer and Parsons (24), to be 0.6990 volt at 25°C. π_m can be found by combining the quinhydrone electrode with a calomel electrode and measuring the voltage exactly as in the case of the hydrogen electrode. To find π_m from the measured voltage, the potential of the calomel electrode must be subtracted, so that we finally have the working equation

$$\text{pH} = \frac{0.6990 - V - 0.2450}{0.059} = \frac{0.4540 - V}{0.059} \quad (5)$$

when the saturated-potassium chloride-calomel half cell is used at 25°C.

The quinhydrone electrode can be used with many solutions that poison the hydrogen electrode (15,21,34). For example, one of the authors found the quinhydrone electrode very useful for measuring the pH value of sewage effluents, which poisoned the hydrogen electrode to such an extent that its use was precluded. On the other hand, the quinhydrone electrode cannot be used with any solution containing any oxidizing or reducing agent which disturbs the equivalence of quinone and hydroquinone. Atmospheric oxygen oxidizes hydroquinone in alkaline solution, and for this reason the electrode cannot be used in solutions of pH value higher than about 8. Other interfering oxidizing agents are ferric, permanganate, and dichromate ions. Some of the reducing agents that interfere are iodide, chromous, and titanous ions. Other substances, as yet uninvestigated, may act similarly, and hence the pH values obtained with a solution of unknown constitution should be checked, wherever possible, by the hydrogen electrode or by the colorimetric method.¹



57.—
Common
form of quin-
hydrone elec-
trode (Leeds
and Northrup
Company).

The common form of quinhydrone electrode (28), shown in Fig. 57, consists of a gold wire wound around the end of a glass tube and sealed to a platinum wire that is sealed into the tube and makes contact with mercury, into which the wire leading to the potentiometer dips. This electrode is dipped into the solution whose pH is to be measured, as is the capillary side arm of the calomel electrode. A little quinhydrone is dissolved in the solution, and the voltage of the cell so formed is measured with a potentiometer. The pH value is then found by applying Eq. (5) above.

THE GLASS MEMBRANE ELECTRODE

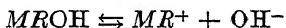
When a cell consisting of two compartments separated by a thin glass membrane is filled with two solutions of different hydrogen-ion concentration, a potential is set up across the

¹Since this chapter was written, Wallace and Beek (*Bur. Stand. J. Res.*, 4, 737, 1930) have shown that the pH values obtained for tan liquors with the quinhydrone electrode differ widely from those obtained with the hydrogen electrode. A slight difference, capable of correction by applying a factor, was found in water extracts of vegetable-tanned leathers.

membrane which depends upon the difference in hydrogen-ion concentration. Such a cell is first calibrated by determining the voltages produced when a buffer solution of constant hydrogen-ion content is placed in one compartment and a series of solutions of different and known hydrogen-ion concentrations are placed in the other. The hydrogen-ion concentration of an unknown solution can then be found by determining the potential between this solution and the standard buffer. Pleass (34) found that this so-called glass electrode could be used to determine pH values in tannery liquors when all other known methods failed. Cameron (8) has just published a valuable description of a suitable potentiometer for use with the glass electrode.

INDICATOR METHOD

There are a very large number of organic compounds which change color characteristically in a definite pH range. These substances are either weak acids or weak bases. Methyl red, for example, is a weak base. Like all weak bases, it dissociates very slightly into hydroxyl ions and positive ions which we may symbolize as MR^+ , according to the equation



When methyl red is dissolved in a solution containing even as low a hydroxyl-ion concentration as 10^{-8} -normal, practically all the indicator is present in the undissociated form. The undissociated methyl red produces a yellow solution. When the hydroxyl-ion concentration of the solution falls still lower, however, an appreciable part of the indicator exists in the form of the ion MR^+ , which gives a red color. When the hydroxyl-ion concentration falls so low that all the indicator is present in the form of the ion, the solution is a pure red. When both the undissociated molecules and the ions are present, the color is a mixture of yellow and red, or orange, the exact shade depending upon the proportion of the two forms.

Increasing the hydrogen-ion concentration always decreases the hydroxyl-ion concentration of a solution. Hence, as the hydrogen-ion concentration of a solution of methyl red is increased, more and more of the dissociated red form of the indicator can exist. At pH values greater than 6.0, practically all the indicator exists in the undissociated state, and the solution is clear yellow. Beginning at pH = 6.0 a little of the red form is present, and

the amount increases as the pH value is lowered, until at pH = 4.4 all the indicator exists in the form of ions, and the solution is clear red, or pink. At any pH value between 6.0 and 4.4, the solution will have a characteristic color that is a mixture of yellow and red. Thus, to determine the pH value of a solution whose pH value is between 4.4 and 6.0, we can add a little methyl red indicator to it and note the color produced. As it is impossible to keep in mind the exact shade corresponding to every pH value in this range, the unknown solution is compared with solutions of known pH value also treated with methyl red. Such solutions are made up to have pH values differing usually by 0.2 pH unit. The unknown solution is compared with the solutions of known pH, and the known solution whose color most nearly matches that of the unknown is ascertained. The pH value of the unknown solution is taken as that of this comparison solution or, if the unknown is clearly intermediate in color between two of the standards, as the intermediate pH value.

Of course, if the unknown solution happens to give a clear red or a yellow color with methyl red, all that can be said is that the pH value is at least as low as 4.4 or at least as high as 6.0, as the case may be. In such a case, another indicator, which changes color over a different pH range, must be employed. Indicators are now available for any pH range from 0.2 to 13.6.

Another theory which has been advanced to explain the color change of indicators is that the molecule of the indicator undergoes an internal structural change, beginning at a definite pH value. Whichever theory is correct, the facts are that above a certain pH value the indicator exists wholly in one form, with a definite color; below a different pH value, the indicator exists wholly in a second form, having a different color (or no color at all, as in the case of phenolphthalein); and at pH values between the two, both forms exist in proportion depending upon the pH value, with a resulting mixed color that is characteristic of the pH value.

CHOICE OF INDICATORS

Hundreds of indicators have been described, but most of them are not suitable for accurate determination of pH value. Some of the criteria governing the selection of indicators are: The indicator must be obtainable in a state of constant purity; there must be a sharp contrast between the colors of the acid and

TABLE 33.—CLARK-LUBS-COHEN

Name	pH range	Color change
Metacresol purple.....	.2 to 2.8	Red to yellow
Thymol blue (acid)....	.2 to 2.8	Red to yellow
Brom phenol blue.....	.0 to 4.6	Yellow to blue
Brom cresol green.....	.8 to 5.4	Yellow to blue
(Methyl red)*.....	.4 to 6.0)	(Red to yellow)
Chlor phenol red.....	.8 to 6.4	Yellow to red
Brom phenol red.....	.2 to 6.8	Yellow to red
Brom cresol purple.....	.2 to 6.8	Yellow to purple
Brom thymol blue.....	.0 to 7.6	Yellow to blue
Phenol red.....	.8 to 8.4	Yellow to red
Cresol red.....	.2 to 8.8	Yellow to red
Metacresol purple.....	.4 to 9.0	Yellow to purple
Thymol blue (alkaline).	.0 to 9.6	Yellow to blue
Cresol phthalein.....	.2 to 9.8	Colorless to red

¹ From Clark's "Determination of Hydrogen Ions," reprinted by permission of Williams and Wilkins Co., publishers.

* Omitted from Clark's latest revision.

TABLE 34.—LAMOTTE CHEMICAL PRODUCTS COMPANY INDICATORS (25)

Name	pH range	Color change
Cresol red (acid) (2S).....	0.2 to 1.8	Red to yellow
Metacresol purple.....	1.2 to 2.8	Red to yellow
LaMotte yellow.....	2.6 to 4.2	Red to yellow
*Alpha (2:4) dinitrophenol....	2.8 to 4.4	Colorless to deep yellow
Brom phenol blue.....	3.0 to 4.6	Yellow to blue
Brom chlor phenol blue.....	3.0 to 4.6	Yellow to blue
Brom cresol green.....	4.0 to 5.6	Yellow to blue
*Gamma (2:5) dinitrophenol..	4.0 to 5.6	Colorless to deep yellow
Methyl red.....	4.4 to 6.0	Red to yellow
Brom cresol purple.....	5.2 to 6.8	Yellow to purple
Chlor phenol red.....	5.2 to 6.8	Yellow to red
Paranitrophenol*.....	5.4 to 7.0	Colorless to deep yellow
Brom thymol blue.....	6.0 to 7.6	Yellow to blue
Phenol red.....	6.8 to 8.4	Yellow to red
Metanitrophenol*.....	6.8 to 8.4	Colorless to deep yellow
Cresol red.....	7.2 to 8.8	Yellow to red
Thymol blue.....	8.0 to 9.6	Yellow to blue
LaMotte purple.....	9.6 to 11.2	Purple to red
LaMotte sulfo orange.....	11.0 to 12.6	Pale yellow to deep orange
LaMotte violet.....	12.0 to 13.6	Red to blue

* Recommended for work in special cases where the ordinary indicators give abnormal colors with the solutions under examination.

alkaline forms (methyl orange is a familiar example of an indicator that does not fulfill this condition); the pH range over which the color change occurs must be neither too extended nor too short (litmus, for example, changes over a range of 3.6 pH units, which makes it far too insensitive); the color of the indicator should be affected as little as possible by the presence of salts, proteins, or other substances; the indicator should be a stable compound, giving solutions that remain unaltered for a reasonably long time. Many workers have compiled lists of the indicators which they consider most suitable for use over all or part of the pH scale. Probably the most authoritative table of indicators is that of Clark, Lubs, and Cohen (11), given in Table 33. The list of indicators recommended by the LaMotte Chemical Products Co. (25) is given in Table 34. This list includes most of the Clark-Lubs-Cohen indicators but has been extended to more acid and more alkaline solutions than those covered by the indicators of Table 33.

The ranges of the individual indicators overlap slightly, which enables the pH value of a solution to be determined with two indicators in many cases, and this should be done whenever possible.

PREPARING INDICATOR SOLUTIONS

It is necessary that the indicator solutions used for testing unknown solutions shall be of exactly the same strength as those used in making up the comparison standards. Only indicators whose purity is guaranteed

TABLE 35.—ALKALI EQUIVALENTS OF INDICATORS¹

Name	Cubic-centimeter of hundredth- normal sodium hydroxide for
Metacresol purple.....	0.1 g. 26.2
Brom phenol blue.....	14.9
Brom cresol green.....	14.3
Chlor phenol red.....	23.6
Brom phenol red.....	19.5
Brom cresol purple.....	18.5
Brom thymol blue.....	16.0
Phenol red.....	28.2
Cresol red.....	26.2
Metacresol purple.....	26.2
Thymol blue (acid or alkaline).....	21.5

¹ See note, Table 33.

by a reliable dealer should be employed. The strength of indicator solutions is generally 0.04 per cent. To prepare the indicator solution, weigh accurately 0.1000 g. of the indicator, and grind it in an agate mortar with the quantity of hundredth-normal sodium hydroxide solution specified above. Transfer the solution quantitatively to a 250-cc. volumetric flask, and make up to volume with distilled water. Keep the solution in a Pyrex bottle or Erlenmeyer flask, stoppered with a cork through which is thrust a 1-cc. pipette graduated in 0.01-cc. units.

When permanent standards are purchased already prepared, it is desirable to use the indicator solutions prepared and sold by the manufacturer of the standards, to make certain that the concentrations are the same as those of the solutions used in preparing the standards.

COMPARISON STANDARDS

To prepare standards for comparison, a series of solutions must be prepared having pH values that differ by steps of 0.2 pH unit. This is a laborious process, and it is perhaps more economical to purchase standards already made up.

In preparing standards, buffer salts are used. These are salts of weak acids or bases, whose solutions change only a little in pH value when small amounts of acid or of alkali are added to them. Among the buffer salts commonly used for preparing standards are potassium acid phthalate, mono- and dipotassium acid phosphate, borates, glycoll, secondary sodium citrate, etc. Solutions containing definite weights of any of these compounds, carefully purified, have very constant and reproducible pH values. For example, twentieth-molar potassium acid phthalate has a pH value of 3.97 at 20°C. By adding increasing amounts of standard hydrochloric acid to this solution, solutions of definite pH values lower than 3.97 can be prepared, and similarly solutions of higher pH value can be made by adding standard sodium hydroxide. The composition of the buffer solutions recommended by Clark and Lubs is given in Table 36. To prepare these buffers the following solutions are required:

- Fifth-molar potassium acid phthalate solution (40.836 g. per liter).
- Fifth-molar potassium dihydrogen phosphate solution (27.232 g. per liter).
- Fifth-molar boric acid solution containing fifth-molar potassium chloride (12.4048 g. of boric acid and 14.912 g. of potassium chloride per liter).
- Fifth-molar sodium hydroxide solution (carbonate free).
- Fifth-molar hydrochloric acid solution.
- Fifth-molar potassium chloride solution (14.912 g. per liter).

The salts employed should be carefully purified by recrystallizing several times. For details, Clark's book (11) should be consulted.

TABLE 36.—COMPOSITION OF MIXTURES GIVING pH VALUES AT 20°C. AT INTERVALS OF 0.2 pH UNIT¹

Potassium chloride — hydrochloric acid mixtures. Measure the indicated volumes of fifth-molar potassium chloride and fifth-molar potassium chloride mix, and dilute to 100 cc.

pH value	Cubic centimeter fifth-molar potassium chloride	Cubic centimeter fifth-molar hydrochloric acid
1.0	0.00	59.5
1.1	2.72	47.28
1.2	12.45	37.55
1.3	20.16	29.84
1.4	26.30	23.70
1.5	31.18	18.82
1.6	35.03	14.95
1.7	38.12	11.88
1.8	40.57	9.43
1.9	42.51	7.49
2.0	44.05	5.95
2.1	45.27	4.73
2.2	46.24	3.76

Phthalate — hydrochloric acid mixture. To 50 cc. of fifth-molar potassium acid phthalate add the indicated quantity of fifth-molar hydrochloric acid and dilute to 200 cc. with carbonate-free distilled water.

pH value	Cubic centimeter of fifth-molar hydrochloric acid	pH value	Cubic centimeter of fifth-molar hydrochloric acid
2.2	46.60	3.2	14.80
2.4	39.60	3.4	9.95
2.6	33.00	3.6	6.00
2.8	26.50	3.8	2.65
3.0	20.40		

¹ See note, Table 33.

TABLE 36.—COMPOSITION OF MIXTURES GIVING pH VALUES AT 20°C AT INTERVALS OF 0.2 pH UNIT.—(Continued)

Phthalate — sodium hydroxide mixtures. To 50 cc. of fifth-molar potassium acid phthalate add the indicated quantity of fifth-molar sodium hydroxide and dilute to 200 cc.

pH value	Cubic centimeter of fifth-molar sodium hydroxide	pH value	Cubic centimeter of fifth-molar sodium hydroxide
4.0	0.40	5.2	29.75
4.2	3.65	5.4	35.25
4.4	7.35	5.6	39.70
4.6	12.00	5.8	43.10
4.8	17.50	6.0	45.40
5.0	23.65	6.2	47.00

Monopotassium phosphate — sodium hydroxide mixtures. To 50 cc. of fifth-molar monopotassium phosphate add the indicated quantity of fifth-molar sodium hydroxide and dilute to 200 cc.

pH value	Cubic centimeter of fifth-molar sodium hydroxide	pH value	Cubic centimeter of fifth-molar sodium hydroxide
5.8	3.66	7.0	29.54
6.0	5.64	7.2	34.90
6.2	8.55	7.4	39.34
6.4	12.60	7.6	42.74
6.6	17.74	7.8	45.17
6.8	23.60	8.0	46.85

Boric acid, Potassium Chloride — Sodium Hydroxide mixtures. To 50 cc. of a solution containing fifth-molar boric acid and fifth-molar potassium chloride add the indicated quantities of fifth-molar sodium hydroxide, and dilute to 200 cc.

pH value	Cubic centimeter of fifth-molar sodium hydroxide	pH value	Cubic centimeter of fifth-molar sodium hydroxide
7.8	2.65	9.0	21.40
8.0	4.00	9.2	26.70
8.2	5.90	9.4	32.00
8.4	8.55	9.6	36.85
8.6	12.00	9.8	40.80
8.8	16.40	10.0	43.90

The pH value of each solution should be checked by means of the hydrogen electrode and brought to the exact pH specified by adding a little more sodium hydroxide or a little hydrochloric acid, as required.

The standard buffer solutions should be kept in resistance glass bottles, carefully stoppered. To prepare standard tubes from these solutions, pipette exactly 3.0 cc. of each solution whose pH value falls in the range of a given indicator into a clear glass tube measuring about 9 by 100 mm. All the tubes must be of uniform diameter and thickness of wall. For example, in preparing standard tubes for use with cresol red (pH range = 7.2 to 8.8) pipette 3.0-cc. portions of buffers of pH values 7.2 to 8.8, making nine tubes. To each solution add exactly 0.30 cc. of the indicator solution. Seal off each tube with the blast lamp, and label it with the name of the indicator and the pH value.

In using standards so prepared, 3.0 cc. of the unknown solution and 0.3 cc. of the indicator are employed. Of course, 5.0 cc. of buffer solution and 0.5 cc. of indicator solution could have been used for the standards, in which case 5.0 cc. of the unknown solution and 0.5 cc. of indicator solution must be used for the test. The all-important point is that the test solution and each of the standards must contain exactly the same quantity of indicator in the same volume of solution and that the diameters of all the tubes must be exactly the same.

THE COMPARATOR

The simplest form of comparator consists of a wooden block in which three holes are bored, into which two standards and the tube of unknown solution can be inserted. A portion of the front and back of the block opposite these holes is cut away, and a piece of ground glass fastened over one opening. The tube containing the unknown solution, with the indicator solution added, is placed in the center hole, and standard tubes of pH values 0.2 unit apart are placed in the holes on either side of the unknown. The block is held against the light so that the light reaches the eye by passing through the tubes transversely. Different standard tubes are tried until a pair is found whose colors lie on either side of that of the unknown.

In order to compensate for turbidity or slight color in the unknown solution, actual comparators have holes for six tubes instead of three. These holes are arranged as shown in Fig. 58.

The color standards are placed in holes *B* and *C*. A tube of distilled water is placed in hole *A*. Three tubes of unknown solution are placed in holes *E*, *D*, and *F*, but indicator is added to tube *D* only. Slots are cut through the block opposite each pair of holes, and light passing through each slot traverses one tube containing indicator and one tube without indicator, likewise one tube containing the turbidity or color of the unknown solution and one tube that is clear and contains only the color of the pure indicator. Hence the light passing through each slot is comparable with that passing through the other slots. This compensation for color is known as the Walpole technic.

A block comparator of this type, manufactured by the LaMotte Chemical Products Co. (25), is shown in Fig. 59. Block comparators of this type are available with sets of standard tubes for each of the indicators listed in Table 34. To cover the whole pH range thus requires about 12 separate block comparators. A more elaborate comparator is the LaMotte roulette comparator (25) shown in Fig. 60. In this compar-

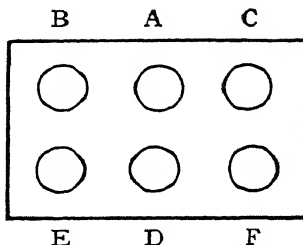


FIG. 58.—Principle of the block comparator.

ator, standard tubes for any four indicators are mounted in a revolving drum, alternating with tubes of distilled water, and the drum is rotated until a color match is obtained. The three tubes of unknown solution are inserted in a fixed part. By means of the roulette comparator, much time can be saved when a larger number of determinations are to be made daily.

The light used with the comparator may be diffused daylight or, better, a so-called daylight lamp.

Determination of pH with the Comparator.—Filter the solution to be examined, and bring it to room temperature. If the pH value of the solution is not known even approximately, place about 1 cc. in several holes of a spot plate, and add a drop of phenol red indicator to one portion. If a red color is produced, the pH value is greater than 8.4. Treat a second portion with one drop of cresol red indicator. An orange shade indicates that the pH value of the solution is somewhere in the pH range covered by cresol red (7.2 to 8.8). To confirm this, test a third portion with one drop of thymol blue indicator. A yellow color indicates that the pH value of the solution is not greater than that of the more acid part of the thymol blue range (8.0 to 9.6). From these preliminary tests, the pH value is shown roughly to

lie somewhere in the pH range 8 to 9, which is covered by the indicators cresol red and thymol blue.

If a yellow color had been produced with phenol red in the first test, showing that the pH value of the solution was less than 6.8, the next indicator to try would have been brom thymol blue, followed by brom cresol purple or brom phenol red, and so on up the list given in Tables 33 and 34.

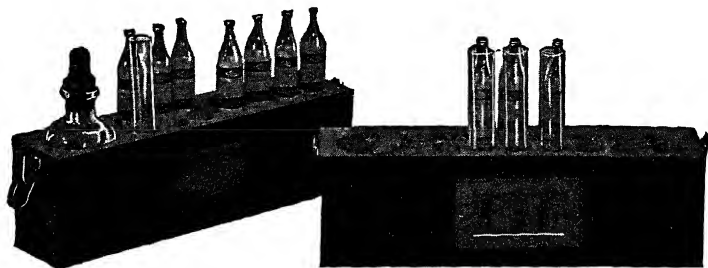


FIG. 59.—Block comparator (LaMotte Chemical Products Company).

Having established that the pH of the solution lies in the range covered by cresol red and thymol blue, pipette exactly 3.0 cc. into each of three tubes, similar in all respects to the standards. (With the LaMotte comparators, fill the graduated tubes to the 10-cc. mark.) Place the tubes in holes *E*, *D*, and *F* of the comparator (Figs. 58 and 59). Pipette exactly 0.3 cc. of

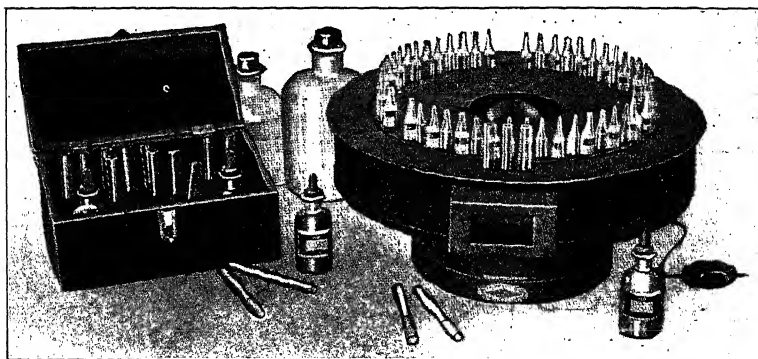


FIG. 60.—Roulette Comparator (LaMotte Chemical Products Company).

cresol red indicator into tube *D* (0.5 cc. with the LaMotte apparatus), and mix. Place a standard tube of distilled water in hole *A*. Select two standard tubes containing cresol red, differing in pH value by 0.2, whose colors seem closest to that of the unknown solution (tube *A*), and place them in

holes *B* and *C*. Hold the comparator up to the light and examine the colors. Change the tubes in *B* and *C* until either an exact match is obtained between the unknown and one of the standards, or else two tubes are found, differing by 0.2 pH unit, one of which is a little redder than the unknown and the other a little yellower. In such a case, report the pH value of the unknown as that intermediate between those of the standards.

Repeat the determination, using thymol blue if the pH value found with cresol red is greater than 8.0, or phenol red if less than 8.0. The value found with the second indicator should check that found with the first within 0.2 pH unit.

OTHER FORMS OF PERMANENT STANDARDS

In place of standard buffer solutions containing indicators, glass plates of different shades have been recommended as standards for determining pH value. One danger in using colored solutions as indicators is that the colors may change on long standing due to fading of the indicator or alteration of the pH of the solution. (The guaranteed life of standards sold by manufacturers of pH determination equipment is generally one year.) The glass slides are not susceptible to change, but, on the other hand, it is exceedingly difficult to obtain the same optical effect with glass as with a solution and somewhat difficult to reproduce any given color exactly in slides made at different times.

METHODS NOT INVOLVING PERMANENT STANDARDS

Cameron's Titration Method.—An ingenious method for dispensing with permanent standards was described by Cameron (8). In preparing permanent standards, definite quantities of standard sodium hydroxide are added to a fixed amount of buffer salt, giving a series of solutions of fixed pH value. Since the quantity of sodium hydroxide required to produce a certain pH value, say with monosodium phosphate, is known, we can determine the pH value of an unknown solution by determining how much sodium hydroxide it is necessary to add to a given amount of phosphate in order to obtain a solution whose color matches that of the unknown when both are treated with the proper indicator. Having determined the volume of sodium hydroxide required, the pH value can be read off directly from tables such as Table 36.

Cameron's procedure is as follows: Select three Nessler tubes approximately 16 to 17 mm. in diameter, such that 50 cc. of liquid stands at the same height in all. Prepare tenth-molar potassium acid phthalate solution,

tenth-molar potassium dihydrogen phosphate solution, tenth-molar boric acid solution, and tenth-molar sodium hydroxide solution (carbonate free), just as described under Comparison Standards, except that the concentration of the buffer solutions is only tenth- instead of fifth-molar. Prepare 0.04-per cent solutions of the following indicators, as previously described: brom phenol blue, methyl red, brom cresol purple, brom thymol blue, phenol red, cresol red, and thymol blue.

Determine the approximate pH value of the solution by spotting with indicators. Pipette exactly 50 cc. of the unknown into each of two Nessler tubes. Dilute about 1 cc. of the appropriate indicator solution to about 5 cc., and add *exactly* 1 cc. of this diluted solution to each tube. Stopper the tubes and mix by inverting. Pipette exactly 25 cc. of one of the buffers into the third tube. The phthalate solution is employed if the expected pH value is between 4 and 6, the phosphate for the range 6 to 8, and the boric acid for the range 8 to 10. Add *exactly* 1.0 cc. of the diluted indicator solution to the buffer. Titrate buffer solution with fifth-molar sodium hydroxide, mixing after each addition of alkali, until the color of the buffer approaches that of the unknown when the tubes are viewed vertically against a white background. Then dilute the buffer solution nearly to 50 cc., and continue adding fifth-molar sodium hydroxide until an exact match is obtained. In obtaining the final match, the standard buffer tube is placed between the two unknown tubes. The final volume of the buffer solution need not be exactly the same as that of the unknowns, since the intensity of color is proportional to the number of molecules of indicator in the column of liquid traversed by the light, and this is the same whether the volume is great or little, as long as the tubes are viewed vertically and their diameters are the same; however, the volume of the buffer should not differ widely from that of the unknowns because of the slight effect of dilution upon the pH value.

The quantity of buffer solution used in this determination is equivalent to exactly one-quarter the amounts used in preparing the standard buffer solutions given in Table 36. Hence to find the pH value of the solution, multiply the volume of added fifth-molar sodium hydroxide by 4, and read the pH value corresponding to the addition of this volume of sodium hydroxide to 50 cc. of the buffer employed, using Table 36. For instance, if potassium dihydrogen phosphate were the buffer, and 3.15 cc. of sodium hydroxide were required to produce the color match, the value 12.60 is obtained on multiplying by 4, and on consulting the section of Table 36 pertaining to phosphate-sodium hydroxide mixtures it is seen that 12.60 cc. of fifth-molar sodium hydroxide produces a pH value of 6.4.

The Cameron method can be used only with colorless solutions.

HYDROGEN-ION COLORIMETER

By means of the Bausch and Lomb hydrogen-ion colorimeter (2, 11), shown in Fig. 61, hydrogen-ion concentration can be determined with great accuracy by the colorimetric method, without the use of any permanent standards except a limited number of buffer solutions. It will be recalled from the discus-

sion at the beginning of the description of the indicator method that the color of an indicator at any pH value in the range in which it undergoes its transformation from the alkali-stable to the acid-stable form is a mixture of the colors of these two forms, determined by the proportion of these two forms present in the solution. If we prepare a solution of $\text{pH} = 7.9$, for example, and add phenol red indicator, half of the indicator will be in the alkali-stable and half in the acid-stable form. If we look through a column of this solution, say 15 mm. long, we note a color, characteristic of a mixture of equal parts of acid-stable and alkali-

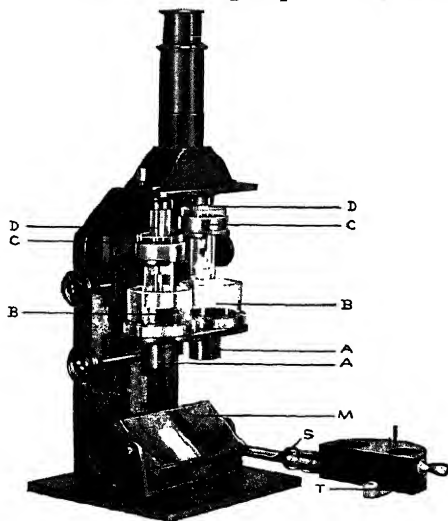


FIG. 61.—Hydrogen-ion colorimeter (Bausch and Lomb Company).

stable phenol red. Now if we prepare a solution of phenol red of $\text{pH} = 5$, all the indicator will be in the acid-stable form; in a solution of $\text{pH} = 11$, all the indicator will be in the alkali-stable form. If we superimpose a column of the acid solution 7.5 mm. long on a column of the basic solution 7.5 mm. long, the color produced is exactly the same as that of the 15-mm. column of the solution containing equal parts of the acid and alkaline forms of the indicator. This fact gives an exceedingly simple and elegant method of determining pH value. By means of the colorimeter, it is possible by varying the lengths of the columns of acid and alkaline forms, keeping the total length constant,

to match the color of a column of solution of any pH value, and from the ratio of the lengths of the acid and alkaline columns, the pH value of the unknown solution may be computed. The construction of the colorimeter is obvious from the illustration and from the following directions for operating it (2).

Testing Illuminations.—Before liquids are introduced into the cups for purposes of comparison, the instrument should be adjusted for even illumination. If sky light is to be used, an unobstructed north window should be chosen and the colorimeter placed directly in front of it. Prepare a comparatively weak solution of a colored inorganic salt, such as a hundredth-normal solution of potassium permanganate. Fill each flare-top cup *C* with the solution approximately to the flare. Rack down the cylindrical cups *B* so that a clearance of 20 to 25 mm. exists below the flare cups. Set the left-hand flare cup at 15 to 20 mm. depth, and take a series of readings with the right-hand cup, raising and lowering it until the two halves of the field viewed through the eyepiece are evenly illuminated. If the average of the readings is not the same as the left-hand setting (within 0.1 or 0.2 mm.), change the position of the colorimeter with reference to the illumination and repeat until a position is found where the right- and left-hand readings are the same. The positions of the colorimeter and the mirror should not be changed from this point on. Remove the colored solutions, and thoroughly rinse and dry the cups *C* and the plungers *D*.

Indicators and Solutions.—The indicator solutions used may be the 0.04-per cent solutions of the indicators listed in Table 33. Prepare a series of stock solutions of pH values from 0 to 12. The solutions need not be accurately standardized. For pH values less than 0, use concentrated hydrochloric acid; for pH = 0, use normal hydrochloric acid; and for pH = 1, use tenth-normal hydrochloric acid. Make up solution of pH values from 2 to 10, as indicated in Table 36. For pH = 11 and 12, dissolve 8.9 g. of disodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, in 500 cc. of water, add 82.6 cc. of tenth-normal sodium hydroxide for pH = 11 and 432 cc. tenth-normal sodium hydroxide for pH = 12, and dilute to 1 l. Whenever possible, these solutions should be checked with the hydrogen electrode; agreement within 0.2 with the nominal pH value is satisfactory. These solutions are used to give the full acid and full alkaline colors of the indicators used in making tests. The solutions giving these colors with the Clark-Lubs-Cohen indicators are given in Table 37.

Reading Clear Liquids.—If the test solution has no body color, the auxiliary cups *A* with their mounts are lifted from the cup carriers and set aside. Determine the approximate pH value of the unknown by spotting to find the indicator which gives neither the full acid nor the full alkaline color with the unknown. Pipette exactly 2.0 cc. of the 0.04-per cent solution of the indicator into each of three 50-cc. volumetric flasks. Fill one flask to the mark with the solution giving the full acid color with the indicator employed, fill the second flask with the solution giving the full alkaline color, and fill the third with the unknown. The concentration of indicator will then be the same in all three solutions, which is fundamentally important. Fill the left-hand cup *C* with the full-acid solution of the indicator. Fill the left-

TABLE 37.—pH VALUES FOR DEVELOPMENT OF FULL ACID AND ALKALINE COLORS OF INDICATORS (2)

Name	pK _a	Acid color pH	Alkaline color pH
Metacresol purple.....	1.51	(Concentrated hydrochloric acid)	6
Thymol blue (acid range).....	1.5	(Concentrated hydrochloric acid)	6
Brom phenol blue.....	3.98	0	7
Brom cresol green.....	4.67	1	8
Chlor phenol red.....	5.98	2	9
Brom phenol red.....	6.16	3	10
Brom cresol purple.....	6.3	3	10
Brom thymol blue.....	7.0	4	10
Phenol red.....	7.9	5	11
Metacresol purple.....	8.32	5	11
Thymol blue.....	8.9	6	12

hand cup *B* with the full-alkaline solution of the indicator. Fill the right-hand cup *C* with the unknown solution containing the indicator. Then move the large cylindrical cups *B* down to some predetermined value on the lower scale. The value on which the table furnished with the instrument is based is 15.0 mm., but any other value may be used, depending upon the strength of the indicator. If another value than 15.0 mm. is used, the pH value must be calculated from the readings mathematically. Then rack down the right-hand cup *C* until it makes contact with *B*. It will be seen that each side of the colorimeter now carries an equal column of liquid, the right being composed entirely of the unknown, and the left of the indicator in alkaline form in *B* and in acid form in *C*. The length of each of these columns is the distance from the bottom of *B* to the bottom of the fixed plungers *D* and is read from the setting of *B* (e.g., 15.0 mm.). The ratio of acid to alkaline color on the left side is varied by moving the left-hand cup *C*. Move the left-hand cup *C* until a color match is obtained. If no match can be obtained, repeat the determination with another indicator.

Reading Colored Liquids.—If the solution has a body color, it must either be removed or balanced. In the Bausch and Lomb design, means are provided to follow the Walpole (11) technic, and balance the body color. The auxiliary substage cups are used to provide equal depths of the unknown colored solution. Make up the solution of unknown with indicator as usual, and fill the right-hand cup *A*. Fill the left-hand cups *B* and *C* with the indicator-buffer solutions as described above. Fill the right-hand cup *B* with distilled water. We now have on the left the adjustable system *B C D* by which the indicator color may be varied, plus a fixed depth of the unknown with its body color. On the right-hand side is an equal depth of liquid, the color being confined to the substage cup where the indicator

color is superimposed upon the body color. Adjustment of the system *B C D* will match the indicator color. Since body color is already matched by virtue of equal column depths in the auxiliary cups, a complete color match is possible. It will be seen that the auxiliary cups must be of constant depth, and consequently the distance at which the stage with the large cups *B* must be set is fixed at the same depth. In the Bausch and Lomb instrument the auxiliary cups are 15.0 mm. in effective depth, and the single rack controlling the cylindrical cups should always be set at 15.0 when the auxiliary cups are being used.¹

Temperature Control.—A removable jacket *I*, Fig. 61, with water inlet and outlet connections, and tapped for thermometer, surrounds the auxiliary cups. The temperature is kept constant by circulating water from a thermostat through this jacket. This control is not necessary except for very refined work.

Mathematical Solution.—If the large cup *B* containing the alkaline form of the indicator is set at *y* mm. depth on the scale, and the color match is obtained when the cup *C* containing the acid form is at *x* mm., it is obvious that the ratio

$$\frac{\text{Alkaline form}}{\text{Acid form}} = y - x$$

pH value is connected with ratio of alkaline to acid form by the equation (11)

where pK_a' is the value at which transformation is just 50 per cent complete. Values for pK_a' for the several indicators are given in Table 37. Values of $\log \frac{(y-x)}{x}$ may be calculated for any given value of *y* by substituting various values of *x*. Then by adding the values of pK_a' for the different indicators, a table may be constructed giving values of pH for all values of *x*, with a given value of *y*. The manufacturers of the instrument provide such a table for use when *y* = 15.0, the column length most commonly employed, and values of $\log \frac{(y-x)}{x}$ for use in constructing tables for other values of *y*.

Cautions.—1. When there is used a value of pK_a' of Table 37, the measurements become automatically standardized to the

¹ The depth of the auxiliary cups can be varied by introducing glass disks of known thickness, furnished by the manufacturer.

system used in the initial evaluation of pK_a' (see Clark, "Determination of Hydrogen Ions"). Furthermore, the validity of calculations made with the equation is limited to systems not distinctly different from the buffer solutions of Clark and Lubs with which these values of pK_a' were obtained. The principle of the instrument is still valid, if, for any particular type of solution, the pK_a' value of the indicator is determined anew. For methods, refer to Clark's book (11).

2. Prepare buffer solutions and indicator solutions exactly in accordance with directions. Solutions made inaccurately or from chemicals not strictly pure cannot give accurate results.

3. Keep all cups and plungers scrupulously clean.

4. In operation be sure that the inner cup on the right is racked down to contact with cup *B*.

NOTE.—If desired, the test solution may be placed in cup *B*, in which case cup *C* is racked up to contact with the plunger.

5. Be sure, when using the auxiliary cups, to have the rack which operates the large cups *B* set at a value equivalent to the depth of the liquid in the auxiliary cups (15 mm.).

6. Before introducing the liquids into the colorimeter be sure that the colorimeter is carefully adjusted for even illumination, and do not subsequently move the stand.

USE OF THE COLORIMETER FOR TANNIN SOLUTIONS

Henrich, working in the authors' laboratory, obtained pH values of solutions of tanning extracts and of used tan liquors by both the hydrogen electrode method and the hydrogen-ion colorimeter. The results are given in Table 38. In the case of extracts, he used the filtered solutions containing 4.0 g. of tannin per liter according to the method of the A. L. C. A. (see Chap. IX). The tan liquors were used without dilution after filtering with kaolin, pretanning the paper as prescribed in the determination of soluble matter. The agreement between the two methods is excellent for extracts, except for suparspruce, where there is some doubt as to the validity of the hydrogen electrode measurement, because of the presence of sulfite compounds. The agreement with liquors is sufficiently close for control purposes.

It may be said that the colorimeter affords no saving in time over the hydrogen electrode, because of the necessity of cleaning

and drying the cups after each determination. The colorimeter is more precise than the comparator and seemingly can be used for solutions too highly colored for use with the comparator but is much less rapid in operation than the latter.

TABLE 38.—COMPARISON OF THE HYDROGEN-ION COLORIMETER AND THE HYDROGEN ELECTRODE WITH TANNIN SOLUTIONS

Liquor	pH value	
	Colorim-eter	Hydrogen electrode
Wattle extract.....	5.07	5.00
Quebracho extract..	4.66	4.66
Sumac extract.....	4.09	4.03
Superspruce extract	3.55	3.02
Tan liquor.....	3.02	3.24
	3.28	3.32
	4.03	4.30
	3.17	3.24
	3.12	3.15
	2.99	2.91

HIGHLY COLORED SOLUTIONS (METHOD OF THOMPSON AND ATKIN) (42)

With very highly colored solutions (*e.g.*, very strong tannin solutions), it is impossible to determine pH directly either with the comparator or with the colorimeter. By diluting such solutions sufficiently, the color can be reduced to a point where measurements of pH can be made colorimetrically, but as pH value always changes on dilution, such measurements are not directly valuable. However, by determining the pH values at a number of different dilutions and plotting the values found against the logarithms of the dilutions, a straight-line graph is obtained, which can be extrapolated to zero dilution, giving the pH value of the undiluted liquor. For a discussion of the principle of this method and working details, Thompson and Atkin's original paper (42) should be consulted.

POTENTIOMETRIC VS. COLORIMETRIC METHODS

The potentiometric method is the more fundamental. pH values can be determined with the hydrogen electrode with greater precision than by any colorimetric method. A precision

better than 0.1 pH unit is, however, seldom necessary in the control of tannery liquors. The potentiometric method can be used for solutions too highly colored to be tested by the comparator or even the colorimeter without the use of the dilution method, which requires several measurements to obtain one value. Both methods are subject to error from interfering substances, the potentiometric from poisoning of the electrode and from oxidation-reduction potentials, and the colorimetric through salt errors, protein errors, dichromatism, etc. The potentiometric method is probably the more subject to *gross* errors, due either to the above causes or to careless manipulation. The indicator methods are undeniably the quicker, especially when a large number of measurements must be made with colorless or slightly colored solutions.

The authors use the hydrogen electrode for routine determinations of pH value of tan liquors, tanning extracts, and chrome liquors and the comparator method for similar measurements with bate liquors, soak liquors, and colorless solutions in general. For investigational work, whichever method appears most convenient is employed, and wherever possible the results obtained are checked by the other method.

POTENTIOMETRIC TITRATIONS

In colored or turbid solutions, in which the end point of a titration cannot be determined with indicators, total acidity or alkalinity may be determined with the hydrogen electrode as follows:

Pipette exactly 50.0 cc. of the solution into the cup (*J*, Fig. 47). Determine pH value. Then set the dials of the potentiometer at a voltage corresponding to pH = 7.0, the neutral point. Titrate with standard acid or alkali, pausing a few seconds after each addition to allow equilibrium to be established, and tap the galvanometer key after each addition, until no deflection occurs, showing that the pH value of the solution is 7.0. Read the volume of added acid or alkali, and calculate total acidity or alkalinity exactly as if an indicator had been used to determine the end point.

References

1. BALL, T. R.: Simple Reference Electrode for Potentiometric Titrations, *Ind. Eng. Chem.*, **19**, 370, 1927.
2. BAUSCH AND LOMB OPTICAL Co.: Private bulletin, 1929.
3. BILMANN, E.: Hydrogenation of Quinone, *Ann. Chim.*, **15**, 109, 1921; Quinhydrone Electrode and Its Applications, *Bull. Soc. Chim.*, **41**, 213, 1927.

4. BILLMANN, E., and H. LUND: The Quinhydrone Electrode, *Ann. Chim.*, **16**, 321, 1921.
5. BLACKADDER, T.: Practical Expression of Effective Acidity, *J. Am. Leather Chem. Assoc.*, **19**, 647-651, 1924.
6. BLACKADDER, T.: Ripening of Hydrogen Electrodes, *J. Am. Leather Chem. Assoc.*, **20**, 17-19, 1925.
7. BRUENNICH, J. C.: Electrometric Titrations, *Ind. Eng. Chem.*, **17**, 631, 1925.
8. CAMERON, D. H.: Derivation of Reference Values for Calomel Electrodes, *J. Am. Leather Chem. Assoc.*, **24**, 80-87, 1929; Hydrogen-ion Concentration by a Modified Colorimetric Method, *ibid.*, **24**, 76-80, 1929; Glass Electrode and Vacuum Tube Potentiometers, *ibid.*, **26**, 7-23, 1931.
9. CAMERON, D. H., and R. SHEARER: Shaker for Clark Hydrogen Electrode Vessels, *ibid.*, **24**, 130-133, 1929.
10. CLAFIN, A.: What the Practical Tanner Should Know about pH, *Leather Manuf.*, **39**, 371, 1928; **40**, 9, 1929; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 321, 1929.
11. CLARK, W. M.: "The Determination of Hydrogen Ions," 3d ed., Williams and Wilkins Co., Baltimore, Md., 1928.
12. CLARK, W. M.: Determination of Hydrogen and Hydroxyl Ions and Their Significance, *J. Am. Leather Chem. Assoc.*, **20**, 544-564, 1925.
13. CORNISH, R. C.: Use of the Hildebrand Electrode in Biological Solutions, *J. Am. Chem. Soc.*, **50**, 3,310, 1928.
14. DAVIS, C. E., and H. M. SALISBURY: Chart of Indicators Useful for pH Measurements, *Ind. Eng. Chem. (Anal.)*, **1**, 92, 1929.
15. DAWSON, L. E.: pH with the Quinhydrone Electrode, *Sugar*, **28**, 211, 262, 310, 369, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 279, 1927.
16. FALES, H. A., and W. A. MUDGE: The Saturated Potassium Chloride-calomel Cell, *J. Am. Chem. Soc.*, **42**, 2,434, 1920.
17. FASOL, T.: Methods and New Electrodes for the Determination of pH Value, *Collegium*, 435, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 443, 1929.
18. GRANGER, F. S., and J. M. NELSON: Oxidation and Reduction of Hydroquinone and Quinone from the Standpoint of Electromotive Force Measurements, *J. Am. Chem. Soc.*, **43**, 1,401, 1921.
19. HARDEN, W. C., and N. L. DRAKE: A New Series of Sulphonphthal-eins, *J. Am. Chem. Soc.*, **51**, 562, 1929.
20. HUGONIN, G.: A New Method for the Determination of Hydrogen-ion Concentration, *Cuir tech.*, **14**, 210, 232, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 46, 1926.
21. HUGONIN, G.: Use of the Quinhydrone Electrode for the Measurement of the Hydrogen-ion Concentration of Tan Liquors, *ibid.*, **13**, 385-392, 1924; *J. Am. Leather Chem. Assoc.*, **20**, 52-73, 1925.
22. KOEHLER, L.: Colorimetric Determination of Hydron Concentration in the Tannery, *Collegium*, 449, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 445, 1929.
23. KUEBELKA, V., and J. WAGNER: Electrometric Determination of Hydrogen-ion Concentration in Colloidal Solutions, Especially Tannery Liquors, *Collegium*, 266-269, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 655, 1927.

24. LAMER, V. K., and T. R. PARSONS: The Application of the Quinhydrone Electrode to Electrometric Acid-base Titrations in the Presence of Air, and the Factors Limiting Its Use in Alkaline Solutions, *J. Biol. Chem.*, **57**, 613, 1923.

25. LAMOTTE CHEMICAL PRODUCTS CO.: "The ABC of Hydrogen-ion Concentration," 5th ed., 1929.

26. LEEDS and NORTROP CO.: *Catalog* 75, 1928; *Bull. Nos.* 755, 765, 766, 768, 1926-1929.

27. McCRUMB, F. R., and W. R. KENNY: Examination of Possible Indicators to Determine the pH of Alkaline Solutions, *Ind. Eng. Chem. (Anal.)*, **1**, 44-46, 1929.

28. McCRUMB, F. R., and W. R. KENNY: Use of Cresol Red in Acid Solution, *J. Am. Chem. Soc.*, **51**, 1,458, 1929.

29. MICHAELIS, L.: "Hydrogen-ion Concentration," Engl. trans. by W. A. Perlzweig, Williams and Wilkins Co., Baltimore, Md., 1926.

30. PARKER, H. C.: New Indicating Equipment for Industrial pH Measurements, *Ind. Eng. Chem.*, **20**, 676, 1928; *Progress in Electrometric Control Methods in Industry*, *ibid.*, **19**, 660, 1927.

31. PARKER, H. C., and C. A. DANNER: New Calomel Half Cells for Industrial Hydrogen-ion Measurements, *ibid.*, **17**, 637, 1925.

32. PARSONS, L. B., and W. F. DOUGLAS: Influence of Sodium Chloride on Colorimetric Determination of pH, *J. Bact.*, **12**, 263, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 284, 1927.

33. PIERCE, W. H., and J. F. FUDGE: Adjustment of Reaction of Indicator Solutions and Its Importance in Determining the Hydrogen-ion Concentration of Slightly Buffered Solutions, *J. Am. Chem. Soc.*, **50**, 1,254, 1928.

34. PLEASS, W. B.: Methods Employed for the Determination of pH Value of Tan Liquors and Lime Liquors, *J. Soc. Chem. Ind.*, **48**, 152T-6T, 1929.

35. POPOFF, S., A. H. KUNG, and R. D. SNOW: Preparation of Hydrogen Electrodes and the Removal of a Common Source of Trouble in Connection with Its Use, *J. Phys. Chem.*, **32**, 1056, 1928.

36. POPOFF, S., and M. J. MCHENRY: Smooth Platinum Wires for Electrometric Titrations in Neutralization Reactions, *Ind. Eng. Chem.*, **20**, 534, 1928.

37. ROSSER, L., and V. MORGENTHAU: Simplified Colorimetric Method for Measuring the Hydrogen-ion Concentration of Small Quantities of Highly Colored or Turbid Solutions, *Chem. Ztg.*, **51**, 302-303, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 545, 1927.

38. SCHLEGEL, J. W., and A. H. STUEBER: Some Sources of Error in the Colorimetric Determination of pH Value, *Ind. Eng. Chem.*, **19**, 631, 1927.

39. SCHOLLENBERGER, C. J.: Improved Calomel Electrode, *ibid.*, **17**, 649, 1925.

40. STASNY, E., ed.: "Gerberchemisches Taschenbuch," 2d ed., 1-31, Theodor Steinkopff, Dresden and Leipzig, 1929.

41. THOMAS, A. W.: Tabulation of Hydrogen- and Hydroxyl-ion Concentrations of Some Acids and Bases, *J. Am. Leather Chem. Assoc.*, **15**, 133-146, 1920.

42. THOMPSON, F. C., and W. R. ATKIN: Dilution Method for the Colorimetric Determination of pH in Colored Solutions, *J. Intern. Soc. Leather Trades Chem.*, **13**, 297-299, 1929.

43. VAN DER HOEVEN, C.: pH Value of Distilled Water, *Collegium*, 440, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 444, 1929.

44. VAN URK, H. W.: Universal Indicator Which Gives the Colors of the Spectrum over a pH Range of 3 to 11.5, *Analyst*, **54**, 254, 1929; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 328, 1929.

45. WILLARD, H. H., and A. W. BOLDYREFF: Simple Reference Electrode for Potentiometric Titrations, *J. Am. Chem. Soc.*, **51**, 471, 1929.

46. WILSON, J. A.: "The Chemistry of Leather Manufacture," 2d ed., 1, 98-128, A. C. S. Mon. Ser., The Chemical Catalog Company, Inc., New York, 1928.

47. WILSON, J. A., and E. J. KERN: Hydrogen Electrode Vessels for Use with Tannery Liquors, *Ind. Eng. Chem.*, **17**, 74, 1925; *J. Am. Leather Chem. Assoc.* **20**, 73-75, 1925.

48. WOLF, K.: Investigation of the Accuracy of the Electrometric Method for Determining pH Value, *Collegium*, 308-321, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 657, 1927.

CHAPTER VIII

BEAMHOUSE MATERIALS AND LIQUORS

The "beamhouse" is the department in the tannery in which skins are soaked, limed, unhaired, and delimed or bated (37). The name comes from the "beam," a convex wooden slab set at angle of 45 deg. with the floor, over which skins are thrown to be fleshed or unhaired or scudded with a knife. Although the beam is nearly obsolete, the operations prior to tanning continue to be known as beamhouse operations, as no other convenient collective name exists. The term "wet work" (German, *Wasserwerk*; French, *travail de rivière*) is sometimes applied to them.

The control of the beamhouse involves the analysis of water, lime, sulfides, calcium chloride, lye, muriatic acid, lactic acid, salt, ammonium salts, enzymes, commercial bating and unhairing mixtures, and used soak, lime, and bate liquors. By lime liquor is meant any liquor used to unhairskins, whether or not it contains lime, the material in most common use. Materials used in curing are also included in this chapter, although curing is not a beamhouse operation.

CURING MATERIALS

The curing and preservation of skins (37) is almost always done with common salt, except where the objects of curing are attained by drying. Sodium sulfate, and mixtures of sodium and calcium chloride, have been found to hydrolyze hide substance less than does common salt, but they have not come into general use as curing materials. The addition of sodium carbonate to curing salt has been advocated. Skins from districts in which anthrax is prevalent must be disinfected. The methods for accomplishing this end are (1) the use of formic acid and mercuric chloride and (2) the use of muriatic acid and sodium chloride. In this chapter we shall discuss the analysis of sodium chloride, sodium sulfate, and mercuric chloride. The analysis of the other materials mentioned above is described under the heading of other operations in which they play a relatively more important part.

SODIUM CHLORIDE (21, 28, 30, 32)

Salt is used in the tannery for many other purposes than curing, especially in pickling skins prior to tanning, in soaking, and in chrome and alum tanning. Salt for each of these purposes must meet practically the same requirements. Salt for tannery use should be practically free from iron and should contain the minimum of insoluble matter, calcium, and magnesium salts. Aluminum sulfate is said to be added to salt as a denaturant in countries in which edible salt is taxed and is thought to be very objectionable because of promoting the formation of salt stains. It is not likely to be encountered in this country.

The authors make it a practice to analyze salt samples for water, insoluble matter, iron, aluminum, calcium, magnesium, total sulfate, and total chloride. From these determinations they calculate and report percentage of water, sodium chloride, sodium sulfate, calcium chloride and sulfate, magnesium chloride and sulfate, iron oxide, and aluminum oxide.

The average composition of samples of salt analyzed in the authors' laboratories during the past 10 years is given in Table 39. The constituent that varies most from sample to sample is water, which ranges from less than 0.1 to more than 5.0 per cent.

TABLE 39.—AVERAGE COMPOSITION OF COMMERCIAL SALT SAMPLES

Constituent	Per cent
Water.....	2.90
Sodium chloride.....	95.50
Sodium sulfate.....	0.00
Calcium chloride.....	0.64
Calcium sulfate.....	0.75
Magnesium chloride.....	0.16
Iron oxide plus aluminum oxide.....	0.03
Insoluble matter.....	0.03

Water.—Weigh accurately about 5 g. into a weighed evaporating dish, and dry overnight at about 105°C., or for several hours at 110°C. Cool in a desiccator, and weigh. Repeat to constant weight. Calculate, and report percentage of water.

$$\text{Per cent H}_2\text{O} = \frac{\text{g. loss in weight} \times 100}{\text{g. sample}}$$

Insoluble Matter.—Weigh accurately about 5 g. (or use the residue from the water determination) into a 600-cc. beaker, and dissolve in about 400 cc. of water. Stir until solution is apparently complete, then let stand with occasional stirring for about 1 hr. If more than traces of insoluble matter are seen to be present, filter the solution through ashless filter paper and

wash the paper with hot water until a portion of the filtrate gives no precipitate when tested with silver nitrate and nitric acid. Ignite the paper and insoluble matter in a weighed platinum dish, cool in a desiccator, and weigh. Calculate and report percentage of insoluble matter.

$$\text{Per cent insoluble matter} : \frac{\text{g. insoluble matter} \times 100}{\text{g. sample}}$$

Examination of Insoluble Matter.—If the percentage of insoluble matter found does not exceed 0.2 or 0.3, this examination is seldom worthwhile. If larger amounts are present, proceed as follows: Treat the insoluble matter in the platinum dish with a few drops of concentrated sulfuric acid and several cubic centimeters of hydrofluoric acid. Evaporate under a hood on a sand bath or asbestos board until sulfuric acid is expelled, then ignite over a burner. Cool in a desiccator, and weigh. Take the loss in weight as *silica*. Calculate and report percentage of silica.

$$\text{Per cent SiO}_2 \quad \frac{\text{g. SiO}_2 \times 100}{\text{g. sample taken for insoluble matter}}$$

Fuse the residue from the hydrofluoric acid treatment, if this residue amounts to as much as 0.0025 g., with about 1 g. of sodium carbonate. Dissolve the fusion in moderately dilute hydrochloric acid. A white, insoluble residue indicates the presence of *barium sulfate* in the salt. Filter, wash free from chlorides, ignite, and weigh as barium sulfate. Calculate and report percentage of barium sulfate.

$$\text{Per cent BaSO}_4 \quad \frac{\text{g. BaSO}_4 \times 100}{\text{g. sample taken for insoluble matter}}$$

Add the filtrate, or the unfiltered solution if barium sulfate is not present, to the filtrate from insoluble matter, and proceed to determine iron, aluminum, and the alkaline earths.

Iron.—To the filtrate from insoluble matter, to which is added the solution obtained as described above, add about 10 cc. of concentrated hydrochloric acid. Add a few drops of bromine water, and boil until the excess bromine is expelled. Add a few drops of methyl red indicator, and add ammonium hydroxide cautiously until the color just changes to yellow. Boil for 2 min. Allow the precipitate to settle. If the amount of precipitate is negligible, filter through ashless paper, and wash about 6 times with hot water. Ignite the paper and precipitate in a weighed crucible, cool in a desiccator, and weigh as iron oxide plus aluminum oxide. Calculate and report as percentage of iron plus aluminum as oxides.

$$\text{Per cent Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 = \frac{\text{g. (Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3) \times 10}{\text{g. sample taken for insoluble matter}}$$

If the amount of precipitate is considerable, filter, wash several times with hot water, and redissolve the precipitate by pouring a little hot, dilute hydrochloric acid on the paper and washing several times with hot water, collecting the solution in the beaker in which the original precipitation was

made. Add iron-free sodium peroxide in small increments until the solution is strongly alkaline. Boil for about 10 min. to decompose the excess peroxide, filter through ashless paper, and wash four times with hot water. Save the filtrate and washings for the determination of aluminum. Redissolve the iron precipitate with dilute hydrochloric acid and reprecipitate ferric hydroxide with ammonia. Wash free from chloride. Ignite the paper and precipitate in a weighed crucible, cool in a desiccator, and weigh as ferric oxide. Calculate and report percentage of iron as oxide.

$$\text{Per cent Fe}_2\text{O}_3 = \frac{\text{g. sample taken for insoluble matter}}{\text{g. sample taken for insoluble matter}}$$

Colorimetric Test for Iron.—If the salt is practically free from insoluble matter, and if the solution gives only a negligible precipitate with ammonia, iron may be determined rapidly as described under the analysis of water, employing a 1-g. sample of salt, or 50 cc. of the solution made up for the determination of chlorides.

Aluminum.—To the filtrate from the sodium peroxide precipitation of iron add hydrochloric acid until the solution is acid. Then precipitate aluminum with ammonia, filter, wash, ignite, and weigh as described above. Calculate and report percentage of aluminum as oxide.

$$\text{Per cent Al}_2\text{O}_3 = \frac{\text{g. sample weighed for insoluble matter}}{\text{g. sample weighed for insoluble matter}}$$

Calcium.—Combine the filtrate from the original precipitation of iron and aluminum with the filtrate from the final precipitation of aluminum. Concentrate if necessary to about 400 cc. Add 15 cc. of saturated oxalic acid solution or 10 cc. of 10-per cent ammonium oxalate solution and heat to boiling. Add ammonia in slight excess, allow the precipitate to settle for at least 1 hr. (better overnight), and filter through Whatman No. 44 paper or its equivalent. Wash 3 times with a 1:10 solution of ammonium hydroxide. Save the filtrate and washings for the determination of magnesium. Ignite the paper and precipitate in a weighed crucible, preferably platinum, at the maximum temperature of a good Meker burner, cool in a desiccator, and weigh quickly. Repeat to constant weight. Calculate percentage of calcium as oxide, and use the figure so obtained in calculating percentage of calcium chloride and sulfate as described below

$$\text{Per cent CaO} = \frac{\text{g. CaO} \times 100}{\text{g. sample taken for insoluble matter}}$$

Magnesium.—Concentrate the filtrate from the precipitation of calcium to about 300 cc., acidify with hydrochloric acid and cool to room temperature. Add 10 cc. of a 10-per cent solution of sodium ammonium hydrogen phosphate. Add ammonium hydroxide, drop by drop, with stirring, until the solution is just alkaline to litmus, let stand 15 min., then add about 10 cc. more. Let the precipitate settle overnight. Filter through a weighed Gooch crucible, and wash thoroughly with very dilute (1:40) ammonium hydroxide. Ignite over a good Meker burner, cool in a desiccator, and weigh as magnesium pyrophosphate. Repeat to constant weight.

Calculate as percentage of magnesium oxide and use the figure so obtained in calculating percentage of magnesium chloride and sulfate, as described below.

$$\text{Per cent MgO} = \frac{\text{g. Mg}_2\text{P}_2\text{O}_7 \times 36.2}{\text{g. sample taken for insoluble matter}}$$

Sulfates.—Weigh accurately about 5 g. of salt, and dissolve in about 300 cc. of water. Filter if necessary, wash the paper free from chlorides, acidify the filtrate with about 10 cc. of concentrated hydrochloric acid, and heat to boiling. Add drop by drop, from a pipette, about 10 cc. of a 10-per cent solution of barium chloride. Allow the precipitate to settle several hours (better overnight). Filter through Whatman's No. 44 paper or its equivalent, and wash free from chlorides with hot water. Dry the paper at about 100°C. Ignite in a weighed crucible heating gently until the paper is completely decomposed, and then with the full heat of a good Bunsen burner,¹ allowing free access of air to the contents of the crucible. Cool in a desiccator and weigh. Repeat to constant weight. Calculate percentage of sulfate as sulfur trioxide and use the figure so obtained in calculating percentage of sodium, calcium, and magnesium sulfate as described below.

$$= \frac{\text{g.}}{\text{g. sample}}$$

Chlorides.—Weigh accurately about 5 g. and dissolve in 1,000 cc. of water in a volumetric flask. Mix thoroughly. Pipette exactly 50 cc. of this solution into a beaker, dilute to about 200 cc., add a few drops of 5-per cent potassium chromate solution, and titrate with tenth-normal silver nitrate. The end point is the formation of a permanent brick-red precipitate. Just before the end point is reached, the precipitate usually begins to form clumps, leaving the supernatant liquor relatively clear. When this point is reached, add the solution dropwise, stirring well after each addition, until the color change from pale yellow to orange red or brick red takes place. Calculate and report percentage of chlorine. Use the figure so obtained in calculating percentage of sodium, calcium, and magnesium chloride as described below.

$$\text{Per cent Cl} = \frac{\text{cc. 0.1-N AgNO}_3 \times 0.3546 \times 20}{\text{g. sample weighed}}$$

Calculation of Distribution of Chlorine and Sulfate.—It is generally desirable to report the constituents of the salt as percentages of the compounds presumably present. Any such distribution of the chloride and sulfate present between sodium, calcium, and magnesium is purely arbitrary, but the following scheme at least leads to uniformity and intelligibility in reports:

Determine and calculate, as above described:

Per cent calcium as CaO; molecular weight = 56.1

Per cent magnesium as MgO; molecular weight = 40.3

¹At the maximum temperature of a good Meker burner there is a danger of decomposing barium sulfate.

Per cent sulfate as SO_3 ; molecular weight = 80

Per cent chloride as Cl ; molecular weight = 35.46

Each 0.1 per cent SO_3 = 0.07 per cent CaO and 0.05 per cent MgO .

If per cent SO_3 : per cent $\text{CaO} \geq 1.0:0.7$, calculate all the calcium as sulfate.

Per cent CaSO_4 = per cent $\text{CaO} \times 2.43$

If the remaining SO_3 : per cent $\text{MgO} \geq 1.0:0.5$, calculate all the magnesium as sulfate.

Per cent MgSO_4 = per cent $\text{MgO} \times 3.0$

Calculate the remaining sulfate as sodium sulfate.

Per cent Na_2SO_4 = per cent $\text{SO}_3 \times 1.77$

Calculate all the chlorine as sodium chloride.

Per cent NaCl = per cent $\text{Cl} \times 1.65$

If, however, per cent SO_3 : per cent $\text{CaO} < 1.0:0.7$, calculate all the sulfate as CaSO_4 .

Per cent CaSO_4 = per cent $\text{SO}_3 \times 1.7$

Calculate the remaining calcium and all the magnesium as chlorides and the remaining chloride as sodium chloride:

Per cent CaCl_2 = per cent $\text{CaO} \times 1.98$

Per cent MgCl_2 = per cent $\text{MgO} \times 2.36$

Per cent NaCl = [per cent Cl - (per cent $\text{CaCl}_2 \times 0.64$) - (per cent $\text{MgCl}_2 \times 0.74$)] $\times 1.65$

Similarly, if per cent SO_3 : per cent $\text{CaO} \geq 1.0:0.7$, but the per cent of sulfur trioxide remaining after deducting the quantity necessary to combine with all the calcium is less than twice the total percentage of magnesium oxide, calculate this remaining sulfate as magnesium sulfate, the remaining magnesia as magnesium chloride, and the remaining chloride as sodium chloride.

Examples:

CaO = 0.85 per cent; MgO = 0.37 per cent; SO_3 = 1.31 per cent; Cl = 57.83 per cent

Per cent SO_3 : per cent CaO = $1.0:0.65$, therefore calculate all calcium as sulfate.

Per cent CaSO_4 = $0.85 \times 2.43 = 2.07$ per cent

Per cent SO_3 combined with Ca = $2.07 - 0.85 = 1.22$ per cent

Per cent SO_3 not combined with Ca = $1.31 - 1.22 = 0.09$ per cent

Per cent residual SO_3 : per cent MgO = 0.24, therefore calculate all remaining sulfate as magnesium sulfate and the remaining magnesia as chloride.

Per cent MgSO_4 = $0.09 \times 1.5 = 0.13$ per cent

Per cent MgO combined with SO_3 = $0.13 - 0.09 = 0.04$ per cent

Per cent MgO not combined with SO_3 = $0.37 - 0.04 = 0.33$ per cent

Per cent MgCl_2 = $0.33 \times 2.36 = 0.78$ per cent

Per cent Cl combined with Mg = $0.78 - 0.33 = 0.45$ per cent

Per cent Cl not combined with Mg = $57.83 - 0.45 = 57.38$ per cent

Per cent NaCl = $57.38 \times 1.65 = 94.68$ per cent

SODIUM SULFATE (GLAUBER'S SALT)

Sodium sulfate is sold either as Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, or as the anhydrous salt. The material should be free from insoluble matter, iron, and free sulfuric acid.

Insoluble Matter, Iron and Aluminum, Calcium, and Magnesium.—Determine just as in sodium chloride.

Sulfates.—Weigh accurately about 5 g., and dissolve in exactly 500 cc. of water in a volumetric flask. Pipette 50 cc. of this solution into a beaker, and determine sulfate as directed under the analysis of sodium chloride. Calculate and report as percentage of anhydrous sodium sulfate and as percentage of Glauber's salt.

$$\text{Per cent Na}_2\text{SO}_4 = \frac{\text{g. BaSO}_4 \times 60.87 \times 10}{\text{g. sample weighed}}$$

$$\text{Per cent Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = \frac{\text{g.} \times 138.05 \times 10}{\text{g. sample}}$$

Chlorides.—Pipette 200 cc. of the solution prepared for the determination of sulfate into a beaker, and determine chlorides by titration with standard silver nitrate solution as directed under analysis of sodium chloride.

Free Acid.—Pipette 50 cc. of the solution prepared for the determination of sulfate into an Erlenmeyer flask, dilute to about 150 cc., and add 2 drops of phenolphthalein indicator. The solution should be colorless and should change to pink on the addition of 1 or 2 drops of tenth-normal sodium hydroxide. If more than this amount of alkali is required, titrate to the formation of a pink color with tenth-normal sodium hydroxide, and calculate percentage of free acid as sulfuric acid.

$$\text{Per cent H}_2\text{SO}_4 = \frac{\text{cc. 0.1-N NaOH} \times 4.}{\text{g. sample weighed}}$$

MERCURIC CHLORIDE (BICHLORIDE OF MERCURY, CORROSIVE SUBLIMATE)

Mercuric chloride is used for disinfecting skins from anthrax-infested regions. A quantitative analysis of the salt is seldom justified. Qualitative tests should be made as follows:

Matter Insoluble in Water.—Shake 1 g. with 100 cc. of water until solution is complete. If an appreciable amount of insoluble matter is present, filter through a weighed Gooch crucible, previously washed with alcohol and with ether and dried at 50°C. Wash the insoluble matter with alcohol, then twice with a little ethyl ether, dry at about 50°C., cool in a desiccator, and weigh. Calculate and report percentage of matter insoluble in water.

Matter Insoluble in Ether (Mercurous Chloride).—Weigh 2 g. and dissolve in about 15 cc. of ethyl ether, stirring well and replacing ether lost by evaporation. The sample should dissolve completely. If not, filter the solution through a Gooch crucible, previously washed with ether and dried

at about 50°C., wash the insoluble matter several times with small quantities of ether, dry at 50°C., cool in a desiccator, and weigh. Calculate percentage of matter insoluble in ether.

SOAK LIQUORS AND SOAKING MATERIALS

Skins are soaked before fleshing, liming, and unhairing, for the purposes of removing blood, dirt, salt, and soluble proteins and of causing the skins to imbibe water and return as nearly as possible to their original physical state (37). In the majority of tanneries, soaking is done with water only. Very hard and dry hides are sometimes soaked in dilute sodium sulfide, sodium hydroxide, or other alkali or in dilute acid (commonly formic), which swell the skin and accelerate the imbibition of water. The use of salt solutions for soaking has been advocated. Numerous specific antiseptics for retarding bacterial growth have been proposed. Among these are chlorine, sodium fluoride, sodium sulfide, mercuric chloride, zinc salts, and sodium or calcium hypochlorite. The latter, as well as numerous organic antiseptics, may be employed with advantage for the periodic disinfection of soak vats.

In this section the analysis of water, sodium and calcium hypochlorites, and used soak liquors is described.

WATER (1, 15, 21, 28, 30)

Water is used by tanneries in enormous quantities, the daily consumption of a medium-sized tannery being comparable to that of a small city. The sanitary characteristics of a tannery water are not very important, although gross contamination, as by sewage, is to be avoided. For the sanitary and bacteriological¹ examination of water, the methods of the American Public Health Association (1) should be consulted. The mineral content of water for tannery purposes is very important. The water should be as free as possible from suspended matter, which will tend to discolor the stock; from iron, which produces highly objectionable stains with vegetable tannins and with some dyes; and from calcium and magnesium carbonates. A very hard water is objectionable because the calcium and magnesium salts form precipitates with tannins, with dyes, and with the soaps often used in fat liquoring.

The routine examination of the water supply is seldom necessary, unless the composition of the supply is subject to fluctua-

¹ See also Chap. V.

tions, as in the case of some river waters. If, as is generally the case, only a single source of supply is available, the purpose of the analysis is to determine whether the nature of the water is such as to necessitate treatment, such as filtration, clarification, or softening, before it is used for some or all of the tannery operations. If such a treatment is put into effect, it then becomes necessary to control it by routine examination of the treated water. If more than one source of water is available, the aim of the analysis is to determine which is the best, taking cost into consideration. The final solution of the problem may consist of using a more expensive water, or a treated water, for the operations in which hardness is objectionable and using a cheaper water, or the untreated water, for the operations in which hardness is of no consequence.

The mineral analysis of water includes the determination of total solids, organic matter, suspended matter, silica, iron, aluminum, calcium, magnesium, sodium, and potassium, sulfates, chlorides, alkalinity or acidity, carbonates, and pH value. In addition, the oxygen consumption test and the determination of total hardness by the soap method are useful.

Total Solids.—Pipette 50 cc. of the water, previously well shaken, into a weighed platinum dish. Evaporate to dryness on the water bath and dry at about 105°C. Cool in a desiccator and weigh. Calculate and report total solids in parts per million (p.p.m.).

$$\text{Total solids (p.p.m.)} = \text{mg. total solids} \times 20$$

Soluble Solids.—Filter about 1 l. of water and use portions of the filtrate for this and subsequent determinations. Pipette 50 cc. into a weighed platinum dish, and evaporate, dry, and weigh as described for total solids. Calculate and report soluble solids (p.p.m.).

$$\text{Soluble solids (p.p.m.)} = \text{mg. soluble solids} \times 20$$

Suspended Matter.—Subtract soluble solids from total solids and report the difference as suspended matter (p.p.m.).

Chlorides.—Pipette 100 cc. of the filtered water, add a few drops of a 5-per cent solution of potassium chromate, and titrate with tenth-normal silver nitrate solution as described under analysis of sodium chloride. Calculate and report chlorine (p.p.m.).

$$\text{Cl (p.p.m.)} = \text{cc. 0.1-N AgNO}_3 \times 35.46$$

Sulfate.—Pipette 100 cc. of the filtered water into a beaker, acidify with hydrochloric acid, and determine sulfate as described under analysis of sodium chloride. Calculate and report sulfate as the sulfate ion, SO_4 (p.p.m.).

$$\text{SO}_4 \text{ (p.p.m.)} = \text{mg. BaSO}_4 \times 4.11$$

Silica.—Measure such a quantity of filtered water as will give about 0.5 g. of residue on evaporation, as calculated from the soluble solids content. Evaporate to dryness on the water bath, moisten the residue with strong hydrochloric acid, and bake at about 120°C. (not higher). Moisten the residue with 10 cc. of concentrated hydrochloric acid, add 50 cc. of boiling water, boil for half a minute, and filter. Wash with hot water until free from chlorides, saving the filtrate and washings for subsequent determinations. Ignite the paper and silica in a weighed platinum dish, cool in a desiccator, and weigh as silica. Calculate and report silica in parts per million.

$$\text{SiO}_2 \text{ (p.p.m.)} = \frac{\text{mg. SiO}_2 \times 1,000}{\text{cc. sample taken for evaporation}}$$

If the silica found exceeds 10 parts per million, treat the ignited residue with a few drops of concentrated sulfuric acid and a few cubic centimeters of hydrofluoric acid, evaporate on a sand bath till sulfuric acid is expelled, and ignite, cool in a desiccator, and reweigh. Take the loss in weigh as silica, and calculate to parts per million.

If the residue left after volatilizing silica exceeds 1 mg., fuse it with a little anhydrous sodium carbonate, dissolve the fusion in hydrochloric acid and add the solution to the filtrate from the silica.

Iron.—Determine iron and aluminum together as oxides, as described under analysis of sodium chloride. Determine iron colorimetrically.

Colorimetric Method (1).—Prepare standard iron solution as follows: Weigh exactly 0.7000 g. of crystalline ferrous ammonium sulfate, dissolve in about 100 cc. of water, and add 5 cc. of concentrated sulfuric acid. Titrate with tenth-normal potassium permanganate until a pink color is produced that is permanent for several minutes. Dilute to exactly 1 l.

$$1 \text{ cc.} = 0.0001 \text{ g. Fe}$$

Measure 100 cc. of water into a casserole, acidify with hydrochloric acid, add a few drops of bromine water, and evaporate to dryness on the water bath. Dissolve the residue in 5 cc. of dilute hydrochloric acid (1:1), and transfer to a Nessler tube. To each of a series of Nessler tubes add 5 cc. of 1:1 hydrochloric acid and 1, 2, 3, . . . 10 cc. of standard iron solution. Make all the solutions to 100 cc., and add to each tube exactly 10 cc. of a 2-per cent solution of potassium thiocyanate. Mix and determine the standard tube that most nearly matches the unknown. Make the comparison at once, as the color fades. If the color of the unknown is more intense than that of the strongest standard, repeat the test using a smaller sample of water; if weaker than the weakest, repeat using 1,000 cc. of water. From the iron content of the standard that matches the unknown, calculate and report iron in parts per million.

$$\text{Fe (p.p.m.)} = \frac{\text{cc. standard Fe solution in standard} \times 100}{\text{cc. sample taken}}$$

Aluminum.—Calculate iron found colorimetrically as ferric oxide, subtract from the total iron oxide plus aluminum oxide, and report the difference as aluminum oxide in parts per million.

$$\text{Al}_2\text{O}_3 \quad \text{p.p.m.} = \frac{\text{mg. oxides weighed} \times 1,000}{\text{cc. water evaporated}}$$

$$\text{Fe}_2\text{O}_3 \text{ (p.p.m.)} = \text{Fe (p.p.m.)} \times 1.43$$

$$\text{Al}_2\text{O}_3 \text{ (p.p.m.)} = (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) - \text{Fe}_2\text{O}_3$$

Calcium, Magnesium.—Determine in the filtrate from iron and aluminum as described under analysis of sodium chloride. Calculate and report parts per million of calcium as oxide and magnesium as oxide.

$$\text{CaO (p.p.m.)} = (\text{mg. CaO} \times 1,000) / \text{cc. sample taken}$$

$$\text{MgO (p.p.m.)} = (\text{mg. Mg}_2\text{P}_2\text{O}_7 \times 362.1) / \text{cc. sample taken}$$

Sodium (and Potassium).—Pipette 100 cc. of filtered water, acidify with hydrochloric acid, and add saturated barium hydroxide solution in quantity sufficient to precipitate all sulfates, iron and aluminum, and carbonates. Filter, wash the precipitate with hot water, and add to the filtrate an excess of ammonium carbonate solution and a few drops of ammonium oxalate solution. Heat to boiling, filter, wash the precipitate with hot water, and evaporate the filtrate to dryness. Gently ignite the residue until all ammonium salts are volatilized. Take up the residue with hot water, add a few drops of ammonium carbonate solution, and filter if a precipitate is formed. Evaporate the filtrate to a convenient bulk, transfer the solution to a weighed platinum dish, evaporate to dryness, and ignite gently until all ammonium salts are volatilized. Desiccate, cool, and weigh as sodium chloride. Calculate and report parts of sodium per million.

$$\text{Na (p.p.m.)} = \text{mg. NaCl} \times 3.93$$

Potassium, if present, is weighed with sodium. If the potassium content is desired, determine potassium by the perchlorate method as described under analysis of potassium titanium oxalate (Chap. XII). Deduct from the sodium found above.

pH Value.—Determine the pH value of the water by means of either the hydrogen electrode or the colorimetric method, as described in Chap. VII. The latter applied to water, is sufficiently accurate for practically every purpose.

Hydroxide, Carbonate, and Bicarbonate.—Measure 250 cc. of filtered water, add 5 drops of phenolphthalein indicator, and titrate with tenth-normal sulfuric acid until the pink color is just discharged. Call the volume added *A*. Add 5 drops of methyl orange indicator, and titrate with tenth-normal sulfuric acid until the color is midway between orange and red. To assist in determining the end point, place 250 cc. of distilled water in each of 2 titrating vessels, add to each 5 drops of the indicator and to 1 vessel 1 drop of tenth-normal sodium hydroxide, to the other 1 drop of tenth-normal sulfuric acid. Titrate the water until its color is midway between those of the comparison solutions. Call the further volume of acid required *B*. Calculate and report percentage of hydroxyl ion and carbonate ion, or carbonate ion and bicarbonate ion, in parts per million.

If $A > B$

$$\begin{aligned}\text{OH (p.p.m.)} &= (A - B) \times 6.8 \\ \text{CO}_3 \text{ (p.p.m.)} &= B \times 24\end{aligned}$$

If $A = B$

$$\text{CO}_3 \text{ (p.p.m.)} = 2A \times 12$$

If $A < B$

$$\begin{aligned}\text{CO}_3 \text{ (p.p.m.)} &= A \times 24 \\ \text{HCO}_3 \text{ (p.p.m.)} &= (B - A) \times 24.4\end{aligned}$$

Total Alkalinity, or "Temporary Hardness," as Calcium Carbonate.—From the volume of tenth-normal sulfuric acid required to neutralize 250 cc. of water to methyl orange, determined above, calculate total alkalinity in parts of calcium carbonate per million. This is defined as the temporary hardness of the water.

$$\text{Temporary hardness (CaCO}_3\text{, p.p.m.)} = (A + B) \times 20$$

Total Hardness (Soap Method). *Standard Calcium Solution.*—Weigh exactly 0.2000 g. of pure CaCO_3 into a small beaker, add about 10 cc. of water, cover with a watch glass, and introduce about 2 cc. of strong hydrochloric acid. Boil until effervescence ceases, remove the cover, rinse down the sides and cover, and evaporate to dryness on the water bath. Dissolve the residue in water and evaporate to dryness twice more. Dissolve in water and make up to 1 l.

Standard Soap Solution.—Weigh roughly 12 g. of dry castile soap, dissolve in about 1 l. of 80-per cent pure ethyl alcohol, and let stand several days. Pipette exactly 20 cc. of standard calcium solution and 30 cc. of recently boiled distilled water into a 250-cc. glass-stoppered bottle. Add the soap solution from a burette, about 0.2 cc. at a time, shaking after addition, until a lather forms and remains unbroken for 5 min. after the bottle has been placed on its side. Calculate the volume of the soap solution required to make 1 l. of solution such that 6.4 cc. is required to give a lather with 20 cc. of standard calcium solution (= cc. required for titration $\times 1000/6.4$) and measure this volume and dilute to 1 l. with 70-per cent pure ethyl alcohol.

Determination.—Pipette 50 cc. of water into a 250-cc. glass-stoppered bottle, and titrate with standard soap solution, added from a burette 0.2 cc. at a time, until a lather forms that remains unbroken for 5 min. with the bottle lying on its side. If the volume required exceeds 7.0 cc., repeat the experiment using 25 cc. of water diluted to 50 cc. with distilled water, and multiply the titration obtained by 2. Calculate and report total hardness as parts of calcium carbonate per million by means of the table on p. 231:

Oxygen Consumption (1). *Standard Potassium Permanganate Solution.*—Dissolve about 0.5 g. of pure potassium permanganate in about 1,000 cc. of water. Measure exactly 10 cc. of standard oxalate solution, dilute to 100 cc., add 5 cc. of dilute sulfuric acid, heat nearly to boiling, and titrate with the permanganate solution till a permanent pink color is produced. Measure exactly 100 cc. of the permanganate solution for each 1.0 cc. consumed in the titration, and make up to exactly 1,000 cc.

Standard Oxalate Solution.—Weigh exactly 0.8880 g. of pure ammonium oxalate, and dissolve in exactly 1,000 cc. water.

TABLE 40.—TOTAL HARDNESS IN PARTS PER MILLION OF CALCIUM CARBONATE FOR EACH 0.1 CC. OF SOAP SOLUTION WHEN 50 CC. OF THE SAMPLE IS TITRATED (1)

Cubic centimeters of soap solution	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.0	0.0	1.6	3.2
1.0	4.8	6.3	7.9	9.5	11.1	12.7	14.3	15.6	16.9	18.2
2.0	19.5	20.8	22.1	23.4	24.7	26.0	27.3	28.6	29.9	31.2
3.0	32.5	33.8	35.1	36.4	37.7	39.0	40.3	41.6	42.9	44.3
4.0	45.7	47.1	48.6	50.0	51.4	52.9	54.3	55.7	57.1	58.6
5.0	60.0	61.4	62.9	64.3	65.7	67.1	68.6	70.0	71.4	72.9
6.0	74.3	75.7	77.1	78.6	80.0	81.4	82.9	84.3	85.7	87.1
7.0	88.6	90.0	91.4	92.9	94.3	95.7	97.1	98.6	100.0	101.5

Dilute Sulfuric Acid.—Add 100 cc. of pure, concentrated sulfuric acid to 300 cc. of distilled water, and to this solution add potassium permanganate solution, drop by drop, until a faint pink color is produced and remains on standing for several hours.

Determination.—Pipette 100 cc. of water (unfiltered) into a 250-cc. Erlenmeyer flask, add 10 cc. of the special dilute sulfuric acid and exactly 10 cc. of the standard permanganate solution. Place the flask in a bath of boiling water so that the contents are completely submerged, and boil for exactly 30 min. Remove the flask from the water bath, add exactly 10 cc. of standard oxalate solution, and titrate with the permanganate solution until a faint, permanent pink color is produced. The volume of permanganate required to titrate the excess oxalate equals the volume consumed by the water. Calculate and report oxygen consumed in parts per million.

At least 5 cc. of excess permanganate should be present when the ammonium oxalate is added. If the amount taken is insufficient, repeat using a larger quantity.

O_2 consumed (p.p.m.) = cc. standard $KMnO_4$ consumed

SODIUM HYPOCHLORITE (21, 30) (BLEACHING POWDER, LIQUID BLEACH, LABARRIQUE'S SOLUTION)

Sodium hypochlorite is used extensively as a disinfectant and deodorant and is said to find some use for bleaching leather. The analysis consists in the determination of available chlorine. The material is marketed either as a powder containing about 35 per cent available chlorine or as a strong solution containing about 30 per cent.

Available Chlorine. *Tenth-normal Arsenious Acid.*—Weigh accurately 4.59 g. pure arsenic trioxide, and dissolve in about 25 cc. of 20-per cent

sodium hydroxide. Dilute somewhat and neutralize the excess alkali with normal sulfuric acid, using phenolphthalein indicator. Add 500 cc. of water containing 25 g. of pure sodium bicarbonate, neutralize again if the solution turns pink, and make up to exactly 1 l. The resulting solution is approximately tenth-normal.

Determination.—Weigh accurately from a weighing bottle about 10 g. of hypochlorite, dissolve in water, and make up to exactly 1 l. If the sample is liquid, weigh the dry bottle, introduce about 10 cc. of the sample, stopper, weigh, and rinse the sample out of the bottle with a wash bottle.

Pipette 50 cc. of the solution into a beaker, and add exactly 50 cc. of the approximately tenth-normal arsenic solution. Stir well, add a few drops of starch indicator, and titrate the excess arsenic with tenth-normal iodine solution (Chap. XIII), to the production of a permanent blue color. Repeat the determination, using exactly the same volume of arsenic solution but leaving out the bleach. The difference in the 2 titrations is the volume of tenth-normal iodine solution equivalent to the chlorine in the sample. Calculate and report percentage of available chlorine.

$$\text{Per cent available Cl} = \frac{(A - B) \text{ cc.} \times \text{factor of } I_2 \text{ solution} \times 7.092}{\text{g. sample weighed}}$$

A = cc. approx. 0.1-*N* iodine solution required for blank

B = cc. approx. 0.1-*N* iodine solution required for sample

CALCIUM HYPOCHLORITE (CHLORIDE OF LIME, BLEACHING POWDER)

Available Chlorine.—Weigh accurately about 10 g. into an agate mortar, make to a paste with water, and grind up all lumps with the pestle. Dilute with water, allow coarse particles to settle, and decant off the suspension into a 1-l. volumetric flask. Add more water to the coarse residue, and grind again. Repeat till the whole sample has been transferred to the flask as a fine suspension. Make up to the mark. Without allowing the solid matter to settle, pipette 50 cc. of the suspension and determine available chlorine as directed under analysis of sodium hypochlorite. Calculate and report percentage of available chlorine.

USED SOAK LIQUORS (24)

Used soak liquors are seldom examined regularly as a routine procedure. Very frequently, however, it is advisable to examine used soaks to determine whether conditions are such as to cause damage to the stock from the attacks of bacteria, especially if the skins actually have defects attributable to bacterial damage.

In examining soak waters, the determinations that may prove useful include temperature, pH value, total nitrogen, volatile nitrogen (amines and ammonia), sodium chloride, and sodium hydroxide, sulfide, or any other substance added to the soak and known to be present. The results of no one of these determina-

tions is of any value unless it can be compared with the result, or a series of results, obtained on normal soak waters, *i.e.*, soaks used for stock that subsequently showed no damage of any kind. The bacterial count, for example, of soak waters always runs into millions, unless germicides are employed. If the normal upper limit of the count is known, then the count of a suspected soak will tell whether an excessive number of organisms is present, but not otherwise. Similarly, the nitrogen content of the soak tells nothing in itself, for all soak waters contain dissolved nitrogen, and indeed one of the functions of soaking is the removal of soluble and unwanted nitrogenous compounds. If the average nitrogen content of the normal soak is known, then the nitrogen content of the suspected soak may tell whether excessive quantities of hide substance have been dissolved, although it must be remembered that the nitrogen content of normal soaks is extremely variable, depending largely upon how thoroughly the skins were freed from manure, blood, and lymph by washing after flaying or just before soaking.

The determinations given below are merely some of those that seem to have proved useful in some laboratories.

pH Value.—Determine pH value either with the hydrogen electrode or colorimetrically, as described in Chap. VII. The colorimetric method gives results sufficiently accurate for most purposes. Unless acid or alkaline substances have been added, the pH of used soak liquors generally lies between 6.0 and 8.0. The indicators required are phenol red, cresol red, and brom thymol blue.

Bacterial Count.—Determine as directed in Chap. V. Incubate duplicate plates at 37.7°C. and at room temperature, or at 15°C. if a suitable thermostat is available. The soak waters frequently contain a preponderance of species that grow best at the lower temperature.

Total Soluble Nitrogen.—Filter about 250 cc. of the soak liquor. Pipette 200 cc. into a Kjeldahl flask, add 30 cc. of concentrated sulfuric acid, put in a boiling chip, and boil until most of the water is expelled. At this point, the solution darkens. Add 10 g. of sodium- or potassium sulfate, and digest over a small flame until the solution is colorless. Make the solution alkaline, and distill the liberated ammonia into an excess of tenth-normal sulfuric acid, back-titrate the excess with tenth-normal sodium hydroxide, and calculate total soluble nitrogen as nitrogen, as described in Chap. II.

To be of greatest value, the results should be calculated in percentage of the total nitrogen in the skins that has been dissolved. This requires the following data: volume of soak liquor, weight of pack soaked, and percentage of nitrogen in the skins before soaking. The last may be determined as described for leather in Chap. II. While the percentage of nitrogen in individual skins will vary widely, depending upon the water content, the

The following methods are based on those of the A. S. T. M. (2) (C25-29).

Silica.—Weigh accurately about 0.25 g. in the case of a high-calcium lime or 0.5 g. in that of a low-calcium lime into a platinum dish. Add about 5 cc. of water, mix to a thin paste, and add about 10 cc. of concentrated hydrochloric acid. Let stand until the reaction has subsided, then evaporate to dryness on the water bath. Place the dish in an air bath and heat at not higher than 120°C. for 1 hr. Treat the residue with 5 cc. of hydrochloric acid (sp. gr. 1.20), and let stand for a few minutes. Add 5 cc. of water, and heat on the water bath for 10 min. Filter through ashless paper, and wash the insoluble matter 3 times with dilute hydrochloric acid and twice with cold water.

Evaporate the filtrate to dryness. Extract the residue with hydrochloric acid as before, and filter the insoluble matter through a second filter paper. Place both filters in a weighed platinum crucible and ignite. Cool in a desiccator and weigh. Repeat to constant weight. Treat the ignited residue with 5 cc. of water, 5 cc. of hydrofluoric acid, and a few drops of concentrated sulfuric acid, and evaporate to dryness. Ignite to constant weight. Take the loss in weight resulting from the hydrofluoric acid treatment as silica. Calculate and report as percentage of silica and as percentage of calcium silicate,

$$\text{Per cent SiO}_2 = \frac{\text{g. SiO}_2 \times 100}{\text{g. sample}}$$

$$\text{Per cent CaSiO}_3 = \text{per cent SiO}_2 \times 1.93$$

Iron.—Fuse the residue left from the volatilization of silica with a little anhydrous sodium carbonate, dissolve in dilute hydrochloric acid, and add the solution to the filtrate from silica. Add to the solution a few drops of bromine water, and boil until the excess bromine is expelled. Add about 10 cc. of concentrated hydrochloric acid, and dilute, if necessary, to about 250 cc. Heat the solution to boiling, add a few drops of methyl red indicator, and add ammonia slowly until the color changes to yellow. Boil for a few minutes to remove excess ammonia, and filter. Wash the precipitate 2 or 3 times with hot 2-per cent ammonium chloride solution. Preserve the filtrate for the determination of calcium and magnesium. Dissolve the precipitate on the filter with hot dilute hydrochloric acid, receiving the solution in the beaker in which precipitation took place. Wash the paper thoroughly with hot water. Add enough sodium peroxide to make the solution strongly alkaline, and boil 10 min. Filter, keeping the filtrate for the determination of aluminum. Wash the paper four times. Redissolve the precipitate with dilute hydrochloric acid and reprecipitate the iron with ammonia as above. Filter, wash free from chlorides, ignite the precipitate in a weighed crucible, desiccate, cool, and weigh. Calculate percentage of iron as oxide.

$$\therefore \frac{\text{Fe}_2\text{O}_3 \times 1}{\text{g. sample}}$$

Aluminum.—To the filtrate from the final precipitation of iron add enough hydrochloric acid to make the solution acid. Heat to boiling and precipitate aluminum with ammonia as described under the determination of iron. Filter, wash free from chlorides, and unite the filtrate with that from the first precipitation of iron and aluminum. Ignite the precipitate in a weighed crucible, cool, and weigh. Calculate and report percentage of aluminum as oxide.

$$\text{Per cent} \quad \frac{\text{g. sample}}{\text{g. sample}}$$

Total Calcium.—Add a few drops of ammonium hydroxide to the combined filtrates from the precipitation of iron and aluminum, heat to boiling, add 35 cc. of a saturated solution of ammonium oxalate, and continue boiling until the precipitated calcium oxalate becomes granular. Let stand until the precipitate has settled. Filter through fine filter paper, and wash thoroughly with dilute (2-per cent) ammonium hydroxide. Redissolve the precipitate in a little dilute hydrochloric acid, receiving the solution in the beaker in which the original precipitation was made and washing the paper thoroughly with hot water. Reprecipitate with ammonia and ammonium oxalate as above described, filter, and wash free from chlorides. Ignite the filter and precipitate in a covered platinum crucible, cool in a desiccator, and weigh rapidly. Repeat to constant weight. Calculate and report percentage of calcium as oxide.

$$\text{Per cent CaO} = \frac{\text{g.}}{\text{g. sample}}$$

Alternate Method for Calcium.—Precipitate and filter as above described (or use a Gooch crucible). Wash ten times with small quantities of hot water. Transfer the paper (or crucible) and precipitate to the beaker in which the precipitation was made, spreading out the paper against the upper portion of the beaker. Wash the precipitate into the beaker from the paper with a wash-bottle stream, leaving the paper adhering to the upper portion of the beaker. Add 50 cc. of dilute (1:10) sulfuric acid, dilute to 250 cc., and heat to a temperature between 80 to 90°C. Titrate with tenth-normal potassium permanganate until the solution remains pink. Then drop the paper into the beaker and complete the titration by adding the permanganate dropwise until the pink end point is again obtained. Calculate and report percentage of calcium as oxide.

$$\text{Per cent CaO} = \frac{\text{cc. 0.1-N KMnO}_4 \times \text{factor} \times 0.2803}{\text{g. sample}}$$

Magnesium.—Acidify the filtrate from the total calcium with hydrochloric acid, and concentrate the solution to a volume of about 150 cc. To the cold solution add about 10 cc. of 10-per cent sodium ammonium hydrogen phosphate solution, then add ammonia drop by drop with stirring until the solution is just alkaline; let stand 5 min.; then add about 10 cc. more. Continue stirring for several minutes. Allow the precipitate to settle overnight. Filter through a Gooch crucible, and wash thoroughly with

dilute (2-per cent) ammonia. Ignite over a good Meker burner, desiccate, cool, and weigh as magnesium pyrophosphate. Repeat to constant weight. Calculate and report percentage of magnesium as oxide.

$$\text{Per cent MgO} = \frac{\text{g. Mg}_2\text{P}_2\text{O}_7 \times 36.21}{\text{g. sample}}$$

Calcium Sulfate.—Weigh accurately about 1 g. and stir with about 10 cc. of water in a small beaker. Add 15 cc. of dilute (1:1) hydrochloric acid, and heat until solution is complete. Filter, and wash the residue thoroughly with hot water. Dilute the filtrate to 300 cc., and precipitate sulfate as barium sulfate, as directed under analysis of sodium chloride. Calculate and report percentage of sulfate as calcium sulfate.

$$\text{Per cent CaSO}_4 = \frac{\text{g. BaSO}_4 \times 58.32}{\text{g. sample}}$$

Calcium Chloride.—Weigh accurately about 5 g., and treat with about 100 cc. of water in a beaker. Acidify with dilute acetic acid in slight excess, heat nearly to boiling, and add more acid if necessary to maintain slight acidity. Add a few drops of potassium chromate indicator, and add tenth-normal silver nitrate drop by drop until a permanent brick-red precipitate is formed. Calculate and report percentage of chloride as calcium chloride.

$$\text{Per cent CaCl}_2 = \frac{\text{cc. 0.1-}N \text{ AgNO}_3 \times 0.555}{\text{g. sample}}$$

Calcium Carbonate.—Arrange an apparatus as shown in Fig. 62. *A* is a soda-lime tower, *B* is a small stopcock funnel for introducing acid,

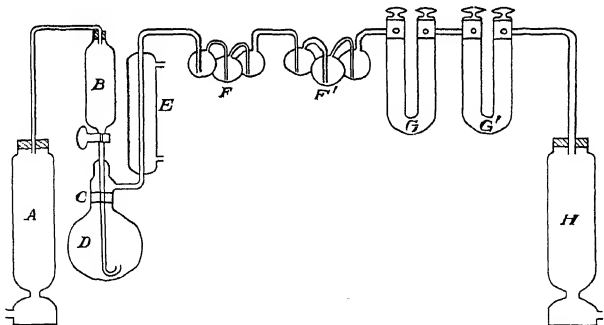


FIG. 62.—Apparatus for determining carbon dioxide in carbonates.

D is a 150-cc. flask. The joint *C* is preferably ground glass. *E* is a small water-cooled condenser for returning to *D* the bulk of the evolved water. *F* and *F'* are Geissler bulbs containing concentrated sulfuric acid. *G* and *G'* are glass-stoppered U-tubes, *G* containing soda lime in both limbs, and *G'* containing soda lime in the left limb and granular calcium chloride in the

right. *H* is a guard tower containing a layer of soda lime and a layer of granular calcium chloride. *H* is attached to an aspirator or suction pump.

In place of sulfuric acid, calcium chloride and phosphorus pentoxide may be used for drying the gas. In place of soda lime, a strong solution of potassium hydroxide protected against loss of moisture by sulfuric acid or calcium chloride, may be used, employing Geissler bulbs instead of U-tubes. If soda lime is used, a Fleming bulb (30) may be used instead of a U-tube.

Weigh accurately about 5 g. of lime, and place in the evolution flask with about 50 cc. of water. Detach the absorption U-tubes, and connect the sulfuric acid bulbs to the guard tower. Draw a slow current of air through the apparatus for about 15 min. Close the stopcock in the separatory funnel. Insert the absorption tubes (previously weighed) in the train, opening the stopcocks. Disconnect *A* from *B*, and place about 50 cc. of dilute (1:1) hydrochloric acid in *B*. Reconnect *A* and *B*. Allow the acid to run into the flask, and as soon as it is all added start the air current. Apply heat to the flask from a small gas flame until the contents boil. Discontinue heating, and continue to draw the air current through the apparatus for about 15 min. Close the stoppers in the absorption tubes, disconnect the tubes from the apparatus, and place them in the balance case for about 15 min. Weigh the tubes, using a similar tube as a counterpoise. Take the total gain in weight of both tubes as carbon dioxide. Calculate and report percentage of carbon dioxide and percentage of calcium carbonate.

$$\text{Per cent CO}_2 = \frac{\text{g. CO}_2 \times 100}{\text{g. sample}}$$

$$\text{Per cent CaCO}_3 = \frac{\text{g. } 22}{\text{g. sample}}$$

Calcium Oxide or Hydroxide.—Calculate the total percentage of calcium oxide combined with silica, sulfate, chloride, and carbonate. Subtract from the total percentage of calcium oxide in the sample, and calculate and report the difference as percentage of calcium oxide (in quicklime) or percentage of calcium hydroxide (in hydrated lime).

$$\begin{aligned} \text{Per cent CaO} &= \text{total calcium as CaO} - (\text{per cent CaCO}_3 \times 0.560) - \\ &\quad (\text{per cent CaSO}_4 \times 0.412) - \\ &\quad (\text{per cent CaCl}_2 \times 0.505) - (\text{per cent CaSiO}_3 \times 0.483) \\ \text{Per cent Ca(OH)}_2 &= \text{Per cent CaO} \times 1.321 \end{aligned}$$

The results found should agree fairly closely with those obtained for available lime determined as directed below. The above calculation involves several arbitrary assumptions, but it has been found that the figures obtained by it are rational and self-consistent.

Available Lime as Calcium Oxide or Calcium Hydroxide (Standard Method of the A. S. T. M., C25-29.—"Available lime" in quicklime or hydrated lime is that (or those) constituent (or constituents) which enters (or enter) into the reaction under the conditions of the specified method or process.

"The interpretation of the results obtained by the following method shall be restricted by the above definition.

"Place 1.4 g. of the carefully prepared and finely ground (passing a No. 100 sieve) lime in a 400-cc. beaker, add 200 cc. of hot water, cover, heat carefully and then boil for 3 min.

"Cool, wash down cover, add 2 drops of phenolphthalein, and titrate with normal hydrochloric acid, adding the acid dropwise as rapidly as possible and stirring vigorously to avoid local excess of acid. When the pink color disappears in streaks, retard the rate of addition of acid somewhat, but continue until the pink color disappears entirely and does not reappear for 1 or 2 sec. Note the reading and ignore the return of color.

"Repeat the test, substituting for the 400-cc. beaker a 1-l. graduated flask fitted with a 1-hole rubber stopper carrying a short glass tube drawn out to a point. Cool, and add dropwise and with vigorous stirring 5 cc. less acid than before. Call the number of cubic centimeters of acid used *A*. Grind up any small lumps with a glass rod flattened at the end, dilute to the mark with freshly boiled distilled water, close the flask with a solid stopper, mix thoroughly for 4 or 5 min., and let settle for 30 min.

"Pipette a 200-cc. portion, add phenolphthalein, and titrate slowly with half-normal hydrochloric acid until the solution remains colorless on standing 1 min. Call the additional number of cubic centimeters *B*. Then the percentage of available calcium oxide is $2A$ plus $5B$. Percentage of available calcium hydroxide is 1.321 times percentage of available calcium oxide.

"NOTE.—To secure accurate and concordant results, it is essential that this method be followed in minute detail. For very accurate work tenth-normal acid may be substituted for half-normal, the calculation then becoming:

$$\text{''Available CaO} = 2A + B.\text{'}$$

Loss on Ignition.—Weigh accurately about 1 g. into a small platinum crucible provided with a cover. Ignite over a good Meker burner, or preferably in a muffle furnace at bright red heat. Desiccate, cool, and weigh. Repeat to constant weight. Calculate and report percentage of loss on ignition.

$$\text{Per cent loss on ignition} = \frac{\text{g. loss on ignition} \times 100}{\text{g. sample}}$$

Water.—Subtract the percentage of carbon dioxide found from the percentage of loss on ignition, and report the difference as percentage of water.

Mechanical Moisture (in Hydrated Lime Only).—The following apparatus is required: (1) a small glass-stoppered flask equipped with 2 ground-in stoppers, one solid for use in weighing, the other carrying an inlet and an outlet tube (Fig. 63); (2) a purification train consisting of (a) a soda-lime tower, (b) a wash bottle containing concentrated sulfuric acid, (c) a phosphorus pentoxide bulb or a second sulfuric acid bottle, (d) the flask (Fig. 63), and (e) a phosphorus pentoxide guard bulb. The whole train is placed in an oven at 120°C. Air is drawn through the train in the order given.

Dry the flask and solid stopper at 120°C., stopper the flask, place it in the balance case until room temperature is attained, and weigh, using a second flask as counterpoise. Introduce into the flask about 3 g. of hydrated lime, stopper, and reweigh. Replace the solid stopper by the one carrying the inlet and outlet tubes, connect the flask to the rest of the train, and draw air through for 2 hr. Detach the flask, quickly close with the solid stopper, and place in or near the balance case until it has cooled to room temperature. Reweigh, using the counterpoise as before. Take the loss in weight as hygroscopic or mechanical moisture, calculate, and report in percentage.

$$\text{Per cent mechanical moisture} = \frac{\text{g.} \quad \text{weight} \times 100}{\text{g. sample}}$$

SODIUM SULFIDE (4, 9, 10, 11, 16, 17, 19, 26, 27, 28, 30, 32, 39)

Sodium sulfide is used as a sharpening agent in unhairing skins and to a lesser extent in soaking dried hides. Two varieties are on the market: lump sulfide, containing from 50 to 60 per cent sodium sulfide, (Na_2S); and crystals, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, containing about 33 per cent. Sodium sulfide is very hygroscopic and is easily oxidized and carbonated on exposure to air. The products of deterioration, which are always present to some extent, are sodium carbonate, thiosulfate, sulfite, and sulfate. Other common impurities are sodium polysulfide and iron sulfide. Iron sulfide is not particularly objectionable in small amounts, since it is insoluble in the alkaline lime liquors but tends to be picked up by and discolor the flesh sides of skins if present in quantity. Polysulfides, thiosulfates, and sulfates are inert. Sodium carbonate and sodium sulfite are undesirable, since they increase the alkalinity of the lime liquor without contributing anything to the sulfide action on the hair. The constituent which gives the material its value is sulfide sulfur.

The complete analysis of commercial sodium sulfide is a complex task, seldom warranted. In the authors' laboratories three determinations only are made: sulfide as sodium sulfide, alkalinity in excess of that due to sodium sulfide, calculated as sodium carbonate, and iron sulfide. Samples of lump sulfide analyzed during the past 10 years have averaged 53.9 per cent sodium sulfide, 7.5 per cent alkalinity (other than that due to sulfide) calculated as sodium carbonate, and 0.45 per cent iron sulfide.

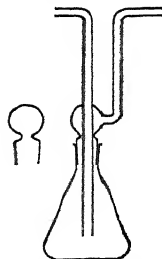


FIG. 63.—Bottle for determination of mechanical moisture (A. S. T. M. Standard Method, C25-29).

Preparation of Sample.—As lump sulfide is very hygroscopic, it is impossible to take a truly representative sample in the usual way without changes taking place that are more serious than any error due to the sample being non-representative are likely to be. The following procedure for taking a grab sample has proved workable: Open the drum, withdraw one or two shovelfuls, and select at random about a dozen lumps of assorted sizes. Break each lump into pieces with a hammer, and from the fragments of each lump select a number of pieces that include both the inner and the outer portions of the lump. Break up all the fragments so selected into particles not larger than 1 mm. in any dimension, mix, and store in a tightly stoppered bottle. Work as rapidly as possible to avoid absorption of carbon dioxide and water from the air.

Sulfide as Sodium Sulfide.—The most convenient method for determining sulfides consists in titrating with standard zinc sulfate containing ammonia and ammonium chloride, using sodium nitroprusside as outside indicator. As long as sulfide is present, this indicator gives an intense blue color when treated with a drop of the solution. The zinc solution precipitates insoluble zinc sulfide, and when the precipitation is complete the color is no longer produced, if the clear supernatant liquor is mixed with the indicator. However, if the portion of solution tested contains zinc sulfide in suspension, a faint color will be produced, because the blue compound formed by sulfide and indicator is more insoluble than zinc sulfide. For this reason, it is necessary to filter the solution before precipitation is quite complete and then complete the titration, using an aliquot of the filtrate. The zinc sulfate solution must contain ammonia and ammonium chloride. Some authors (9) advise adding a constant amount of these reagents to the solution titrated because of the variable amount of zinc sulfate solution consumed in the titration. In analyzing sodium sulfide, however, the volume of standard solution consumed is always great enough to furnish the requisite amount of ammonia (26).

The zinc sulfate method gives results that are accurate within about 1 per cent, which is sufficiently exact for most purposes for which the analysis is desired. If more accurate results are wanted, recourse must be had to the evolution method (30). In this method the sulfide is treated with hydrochloric acid and the evolved hydrogen sulfide is absorbed by ammoniacal zinc sulfate solution, zinc sulfide being precipitated. The determination is completed by determining sulfide in the precipitate by the iodimetric method.

Direct iodimetric titration of the sulfide (21) is not accurate, because sulfites and thiosulfates are titrated along with the sulfide.

Henrich, working in the authors' laboratories, determined sodium sulfide in a strong sulfide strengthening liquor and in numerous lime liquors, by both the zinc titration method and the evolution method. His results, given in Table 42, indicate that the zinc method gives results that do not differ appreciably from those given by the evolution method.

TABLE 42.—COMPARISON OF THE ZINC TITRATION METHOD AND THE EVOLUTION METHOD FOR SULFIDE

Sample of	Volume titrated, cubic centimeters	Cubic centimeters tenth-normal reagent consumed	
		Zinc titration method (tenth-normal zinc sulfate)	Evolution method (tenth-normal iodine)
Used lime liquor.....	25	1.5	1.5
	25	1.5	1.75
	25	2.0	2.1
	25	3.4	3.6
Sulfide strengthening liquor (diluted 1:40) (1).....	10	10.5	10.3
(2).....	10	10.4	10.3
(3).....	10	10.5	

Zinc Sulfate Method (26).—Prepare tenth-normal zinc sulfate as follows: Weigh exactly 28.75 g. of pure crystalline zinc sulfate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and dissolve in about 500 cc. of water in a 1-l. volumetric flask. Add 50 g. of ammonium chloride and 50 cc. of concentrated ammonium hydroxide. Make up to volume, and mix well. If the zinc sulfate is of good grade, the resulting solution is exactly tenth-normal and need not be standardized. If it is desired to standardize the solution, determine zinc by any of the standard methods (30).

Weigh accurately about 5 g. of sodium sulfide and dissolve in 1 l. of water in a volumetric flask. Allow the insoluble matter to settle. Pipette exactly 50 cc. of the solution into a 250-cc. Erlenmeyer flask. Weigh about 0.1 g. of sodium nitroprusside, and dissolve in 100 cc. of water. This solution must be prepared afresh each day. Place small drops of the indicator solution in the holes of a spot plate. Titrate the sulfide solution with tenth-normal zinc sulfate, transferring a drop of the solution to the spot plate after each addition until only a faint blue color is produced, which remains nearly the same when more zinc sulfate solution is added. Note

the volume of zinc sulfate solution added. Pipette exactly 50 cc. of sulfide solution into a 250-cc. volumetric flask, and add 5 cc. less zinc sulfate solution than the volume consumed in the preliminary titration. Make up to the mark, and filter through folded filter paper, using a dry filter paper and receiver. Discard the first 25 cc. of filtrate. Pipette exactly 50 cc. of filtrate into an Erlenmeyer flask, and add tenth-normal zinc sulfate drop by drop, testing the solution by spotting after each addition, until the blue color is no longer produced. Calculate and report percentage of sodium sulfide.

$$\text{Per cent Na}_2\text{S} = \frac{(A + 5B) \times 7.8}{\text{g. sample weighed}}$$

A = cc. 0.1- N ZnSO_4 added before filtering

B = cc. 0.1- N ZnSO_4 added to aliquot after filtering

Evolution Method (30).—Prepare ammoniacal zinc sulfate solution as follows: Weigh approximately 70 g. of crystalline zinc sulfate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and dissolve in about 1 l. of water. Add ammonia until the precipitate which forms at first has redissolved.

Assemble the apparatus as shown in Fig. 64. A is a 500-cc. Erlenmeyer flask closed with a 2-hole rubber stopper. B is a connecting bulb. C is a stopcock funnel for introducing the acid, with a stem reaching nearly to the bottom of the flask. D , E , and F are absorption bottles, containing ammoniacal zinc sulfate solution.

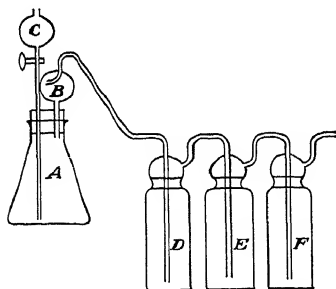


FIG. 64.—Apparatus for determining sulfides by evolution.

Weigh accurately about 10 g. of sodium sulfide, and dissolve in 1 l. of water in a volumetric flask. Pipette exactly 50 cc. of this solution into the evolution flask. Place about 50 cc. of ammoniacal zinc sulfate solution in each of the 3 absorption bottles. See that all connections are tight. Place 100 cc. of a 1:4 solution of sulfuric acid in the stopcock funnel. Open the stopcock, and let the acid run slowly into the flask. Close the stopcock until the reaction has subsided, then open it, and boil the solution vigorously for 20 min. Disconnect the 3 ab-

sorption bottles, and pour their contents into a 500-cc. Erlenmeyer flask, rinsing each bottle and connections several times with distilled water. Add from a burette exactly 100 cc. of approximately tenth-normal iodine solution (Chap. XIII), acidify with hydrochloric acid, and titrate the excess iodine with tenth-normal sodium thiosulfate, using starch indicator. Call the volume of thiosulfate required B . Determine the volume of tenth-normal thiosulfate consumed by 100 cc. of approximately tenth-normal iodine. Call this volume A . Calculate and report percentage of sulfide as sodium sulfide from the equation

$$\text{Per cent} = \frac{(A - B) \times 7.81}{\text{g. sample weighed}}$$

Excess Alkalinity as Sodium Carbonate.—Pipette 50 cc. of the solution prepared for the determination of sodium sulfide into a beaker, and dilute to about 150 cc. Add exactly 50 cc. of tenth-normal sulfuric acid, and boil till hydrogen sulfide is completely expelled. Cool to room temperature, add 2 drops of methyl red indicator, and titrate the excess acid with tenth-normal sodium hydroxide. From the net volume of acid consumed, calculate percentage of total alkalinity as sodium carbonate. Calculate percentage of sodium carbonate equivalent to the sodium sulfide present, subtract from the total alkalinity, and report the difference as percentage of excess alkalinity as sodium carbonate. Any sodium sulfite present will be included.

$$\text{Per cent excess alkalinity as Na}_2\text{CO}_3 = \frac{(50 - \text{cc. 0.1-N NaOH}) \times 10.6}{\text{g. sample weighed}} - (\text{per cent Na}_2\text{S} \times 1.36)$$

Iron Sulfide.—Weigh accurately about 1 g. of sulfide, dissolve in about 200 cc. of water, and filter through ashless paper. Wash the paper thoroughly with hot water. Treat the residue on the paper with hot, dilute hydrochloric acid, and wash free from chlorides. Place the filtrate on the hot plate till hydrogen sulfide is all expelled. Precipitate iron in the filtrate with sodium peroxide or with ammonia after oxidation with bromine water, as described under analysis of sodium chloride. Ignite and weigh as ferric oxide. Calculate and report percentage of iron sulfide.

$$\text{Per cent FeS} = \frac{\times 110.0}{\text{g. sample weighed}}$$

Other Insoluble Matter.—If the filter paper used for filtering iron sulfide is intact, ignite in a weighed crucible, cool, and weigh. Calculate percentage of insoluble matter exclusive of iron sulfide. If the filter paper is punctured during the solution of iron sulfide in acid, determine other insoluble matter in a separate sample, by dissolving in dilute acid, filtering, igniting, and weighing. Calculate and report percentage of insoluble matter (exclusive of iron sulfide).

$$\text{Per cent other insoluble matter} = \frac{\text{g. insoluble matter} \times 100}{\text{g. sample weighed}}$$

BARIUM SULFIDE

Barium sulfide is sometimes used instead of sodium sulfide in unhairing. It is commonly manufactured by reducing barytes with carbon and frequently contains enough carbon to render it black. Aside from the examination of the insoluble matter, the analysis of barium sulfide is much like that of sodium sulfide.

Insoluble Matter.—Weigh accurately about 5 g., and dissolve in about 200 cc. of water. Filter through a Gooch crucible, previously dried at 105°C. and weighed, and wash until the washings no longer give a precipitate when tested with sulfuric acid. Make the filtrate up to 1 l., and use a portion of this solution for determining sulfides.

Dry the crucible and residue at 105°C., cool in a desiccator, and weigh. Calculate and report percentage of insoluble matter.

$$\text{Per cent insoluble matter} = \frac{\text{g. insoluble matter} \times 100}{\text{g. sample}}$$

Barium Carbonate, Iron Sulfide, Carbon, and Barium Sulfate.—Place the Gooch crucible containing insoluble matter in a filter funnel, and treat the contents 3 times with about 10 cc. of warm dilute hydrochloric acid, sucking dry after each treatment. Then wash 4 times with hot water, dry at 105°C., cool in a desiccator, and weigh. Determine iron in the filtrate as directed under analysis of sodium sulfide. Calculate as percentage of iron sulfide, and subtract from the percentage of loss in weight of the insoluble matter on treatment with hydrochloric acid. Take the difference as barium carbonate. Ignite the crucible and residue at bright red heat, cool in a desiccator, and weigh. Take the loss in weight as carbon. Calculate in percentage. Take the residue after ignition as barium sulfate, and calculate in percentage.

$$\text{Per cent FeS} = \frac{\text{g. Fe}_2\text{O}_3 \times 110.1}{\text{g. sample}}$$

$$\text{Per cent BaCO}_3 = \left(\frac{\text{g. loss in weight} \times 100}{\text{g. sample}} \right) - \text{per cent FeS}$$

$$\text{Per cent C} = \frac{\text{g. loss on ignition} \times 100}{\text{g. sample}}$$

$$\text{Per cent BaSO}_4 = \frac{\text{g. residue after ignition} \times 100}{\text{g. sample}}$$

Barium Sulfide.—Determine as directed under analysis of sodium sulfide, using 50 cc. of the filtered solution made up for the determination of insoluble matter. Calculate and report percentage of barium sulfide.

$$\text{Per cent BaS} = \frac{\text{cc. 0.1-N ZnSO}_4 \times 16.94}{\text{g. sample weighed for determination of insoluble matter}}$$

CALCIUM SULFIDE OR SULFHYDRATE

Calcium sulfide is difficultly soluble and hence finds little use in unhairing. Calcium sulphydrate, made by saturating a suspension of lime with hydrogen sulfide, is very soluble. A strong solution of calcium sulphydrate, containing an excess of lime in suspension, has been used as a sharpening agent. Such a solution is analyzed like a used lime liquor, taking into consideration that the sulfide concentration is very much higher.

ARSENIC SULFIDE (7, 28, 32)

Native arsenic sulfide, either orpiment, As_2S_3 , or realgar, is used as a sharpening agent in unhairing. Red arsenic owes its effectiveness entirely to the calcium sulfhydrate formed when it reacts with lime. The analysis consists of the determination of available sulfide and, if desired, of total arsenic, free sulfur, silica, iron and alumina, calcium, and magnesium.

Available Sulfur (32).—Weigh accurately about 0.5 g. of the finely powdered sulfide into a 200-cc. glass-stoppered wide-mouth bottle. Moisten with a few drops of ammonia, and let stand several minutes. Treat with 50 cc. of water and 50 cc. of a suspension of lime containing 5 g. of pure calcium oxide per 100 cc. Stopper and shake in a mechanical shaker until all red particles have disappeared (about 30 min.). Transfer the mixture quantitatively to a 250-cc. volumetric flask, and make up to the mark. Allow the precipitate to settle. Filter through dry filter paper into a dry beaker, discarding the first 50 cc. Pipette 50 cc. of the filtrate into a beaker and determine sulfide by titration with tenth-normal zinc sulfate as directed under analysis of sodium sulfide. Calculate as percentage of sulfur, and report percentage of available sulfide as sulfur.

$$\text{Per cent available S} = \frac{\text{cc. 0.1-N ZnSO}_4 \times 0.8015}{\text{g. sample}}$$

Arsenic (30).—Weigh accurately about 0.2 g., and treat with about 10 cc. of concentrated nitric acid. Heat until solution is complete, then add about 20 cc. of concentrated hydrochloric acid, and evaporate till nitric oxide is expelled completely. Dilute to about 50 cc., filter if necessary, using a very small paper, and wash free from chlorides. The volume of the filtrate and washings must not exceed 100 cc. To the filtrate add 15 cc. of magnesia mixture (55 g. of magnesium chloride plus 70 g. of ammonium chloride plus 650 cc. of water plus concentrated ammonium hydroxide to make 1,000 cc.). Add a few drops of phenolphthalein, and add concentrated ammonia, drop by drop, until the solution becomes pink, then add an additional volume of ammonia equal to one-third that of the neutralized solution. Allow the precipitate to settle for at least 24 hr. Filter through a weighed Gooch crucible, and wash with a 2.5-per cent solution of ammonia until free from chlorides. Suck dry, and dry the crucible and precipitate at about 100°C. Heat at about 400 to 500°C. (dull red heat), preferably in an electric muffle furnace, until ammonia is expelled, then ignite at bright red heat for about 10 min. Cool in a desiccator and weigh. Calculate and report percentage of arsenic.

$$\text{Per cent As} = \frac{\text{g. Mg}_2\text{As}_2\text{O}_7 \times 48.27}{\text{g. sample weighed}}$$

Free Sulfur.—Weigh accurately about 5 g. into an extraction thimble, and extract with carbon disulfide in a Soxhlett apparatus for several hours. If the extraction is done on a hot plate, insert several thicknesses of asbestos

beneath the flask, as carbon disulfide boils at a relatively low temperature. Filter the solution into a weighed crystallizing dish, rinse the flask and filter paper two or three times with a little carbon disulfide, and allow the solvent to evaporate spontaneously under a good hood. Weigh the dish and residue, and calculate percentage of free sulfur.

$$\text{Per cent free S} = \frac{\text{g. sample weighed}}{\text{g. sample weighed}}$$

SODIUM HYDROXIDE (21, 30) (LYE, CAUSTIC SODA)

Sodium hydroxide is sometimes used as a sharpening agent for lime liquors. The principal impurities likely to be present in commercial sodium hydroxide are sodium carbonate, chloride, sulfate, and iron and alumina. Water, which is always present, cannot readily be determined.

Sodium Hydroxide and Carbonate.—Weigh rapidly and accurately about 20 g. of the hydroxide, and dissolve in 1 l. of water in a volumetric flask. Pipette 100 cc. into an Erlenmeyer flask, add a few drops of phenolphthalein indicator, and titrate rapidly with normal sulfuric acid till the pink color just disappears. Call the volume of acid required *A*. Then add a few drops of methyl orange indicator, and continue the titration to the first beginning of a permanent pink color. Call the additional volume of acid required *B*. Calculate and report percentage of sodium carbonate and sodium hydroxide.

$$\text{Per cent NaOH} = \frac{(A - B) \times 40}{\text{g. sample weighed}}$$

$$\text{Per cent Na}_2\text{CO}_3 = \frac{2B \times 53}{\text{g. sample weighed}}$$

Chloride.—Pipette 50 cc. of the solution prepared for the determination of sodium hydroxide and carbonate into a beaker, and make slightly acid with acetic acid. Heat nearly to boiling, and add more acid if necessary to maintain slight acidity. Cool to room temperature, and titrate with tenth-normal silver nitrate, as directed under analysis of sodium chloride. Calculate and report percentage of chloride as sodium chloride.

$$\text{Per cent NaCl} = \frac{\text{cc. 0.1-N AgNO}_3 \times \text{—}}{\text{g. sample weighed}}$$

Sulfate.—Pipette 100 cc. of the solution prepared as described above, acidify with hydrochloric acid, and boil for several minutes to expel carbon dioxide. Dilute to about 300 cc., and precipitate with barium chloride, as directed under analysis of sodium chloride. Calculate and report percentage of sodium sulfate.

$$\text{Per cent Na}_2\text{SO}_4 = \frac{\text{g. BaSO}_4 \times 60}{\text{g. sample weighed}}$$

Iron and Alumina.—Weigh accurately about 5 g., and dissolve in about 200 cc. of water. Acidify with hydrochloric acid, and boil to expel carbon dioxide. If any insoluble matter is present, filter, wash, ignite, weigh, and examine the residue for *silica*. Determine iron and aluminum in the filtrate as directed under analysis of sodium chloride. Report as oxides.

CALCIUM CHLORIDE

Calcium chloride is often used along with strong solutions of sodium sulfide to repress the swelling of the skins. The material is marketed in several forms ("solid," granulated, flake, etc.) containing about 75 per cent calcium chloride and as a solution containing about 50 per cent. The solid form usually contains about 1 per cent sodium chloride, a few tenths per cent calcium hydroxide, and a small amount of insoluble matter.

Insoluble Matter.—Weigh accurately from a stoppered weighing bottle about 5 g. of calcium chloride, and dissolve in about 200 cc. of water. If any insoluble matter is present, filter through ashless paper, and wash with hot water till the residue is free from chlorides. Collect the filtrate in 1-l. volumetric flask, and made to volume for use in later determinations. Ignite the paper and insoluble matter in a weighed platinum crucible, cool in a desiccator, and weigh. Calculate and report percentage of insoluble matter.

$$\text{Per cent insoluble matter} = \frac{\text{g. insoluble matter} \times 100}{\text{g. sample weighed}}$$

Silica, Iron, Aluminum, Calcium, and Magnesium.—Weigh accurately about 1 g. of calcium chloride, and determine exactly as described for the analysis of lime. Calculate and report percentages of silica, ferric oxide, alumina, and magnesium oxide. Calculate percentage of calcium, and use the figure in calculating percentage of calcium chloride, as directed below.

Alkalinity as Calcium Hydroxide.—Weigh accurately about 5 g., dissolve in about 200 cc. of water, add a few drops of methyl orange indicator, and titrate with tenth-normal hydrochloric acid till the color changes to orange red. Calculate and report percentage of alkalinity as calcium hydroxide.

$$\text{Per cent alkalinity as Ca (OH)}_2 = \frac{\text{cc. 0.1-N HCl} \times 0.37}{\text{g. sample weighed}}$$

Calcium Chloride.—Pipette 100 cc. of the filtrate from insoluble matter, made up to 1 l., into a beaker, and determine chlorides by titration as directed under analysis of sodium chloride. Calculate as percentage of chlorine. Calculate the percentage of chlorine required to combine with the sodium and magnesium present, subtract these amounts from the total, and calculate the remainder as calcium chloride. As a check, calculate the percentage of calcium required to combine with the sulfate and hydroxide present, subtract these values from the total calcium percentage, and calculate the remainder as calcium chloride. The results of the two calculations should agree.

$$\text{Per cent Cl} = \frac{\text{cc. 0.1-N AgNO}_3 \times 3.546}{\text{g. sample weighed for determination of insoluble matter}}$$

$$\text{Per cent CaCl}_2 = [\text{per cent Cl} - (\text{per cent MgCl}_2 \times 0.7446) - (\text{per cent NaCl} \times 0.6066)] \times 1.565$$

$$\text{Per cent CaCl}_2 = [\text{per cent Ca} - (\text{per cent Ca(OH)}_2 \times 0.5408) - (\text{per cent CaSO}_4 \times 0.2942)] \times 2.77$$

Calcium Sulfate.—Pipette 100 cc. of the solution prepared as described under determination of insoluble matter, and determine sulfate as directed under analysis of sodium chloride. Calculate and report percentage of calcium sulfate.

$$\text{Per cent CaSO}_4 = \frac{\text{g. BaSO}_4 \times 583}{\text{g. sample weighed for the determination of insoluble matter}}$$

Sodium Chloride.—Weigh accurately about 1 g., and dissolve in about 200 cc. of water. Do not filter. Make the solution slightly acid with hydrochloric acid. Add 0.2 cc. of 10-per cent barium chloride solution for each per cent of sulfur trioxide present, plus a few drops excess. Make the solution alkaline with ammonia, and add about 25 cc. of a 10-per cent solution of ammonium carbonate. Let the precipitate settle. Filter through rapid filter paper, and wash several times with hot water. Set the filtrate aside. Treat the precipitate with about 10 cc. of hot, dilute hydrochloric acid, and catch the filtrate in the beaker used for the precipitation. Wash the paper several times with hot water. Reprecipitate with ammonia and ammonium carbonate as before. Filter, and wash the precipitate free from chlorides. Combine the second filtrate with the first. Evaporate the solution to a small bulk. Transfer to a weighed platinum dish. Evaporate to dryness and heat at dull red heat until all ammonium salts are volatilized. Cool in a desiccator and weigh, repeating to constant weight. Calculate percentage of sodium chloride.

$$\text{Per cent NaCl} = \frac{\text{g. NaCl} \times}{\text{g. sample}}$$

NOTE.—Frequently it will be sufficient to determine insoluble matter, total alkalinity as calcium hydroxide, total chlorides as calcium chloride, and make qualitative tests for sulfate and iron.

USED LIME LIQUORS (5, 6, 8, 9, 14, 18, 23, 24, 25, 26, 28, 32, 33, 34, 35)

The analysis of used lime liquors may be undertaken with one of two ends in view. If the liquor is to be strengthened and used again, the purpose of the analysis may be simply to determine how much of the unhairing agents are left, in order to calculate how much of them to add to restore the liquor to its desired strength. The determinations required for this type of analysis depend, of course, on what unhairing agents are employed. In

the case of a liquor containing lime sharpened with sodium or other sulfide, the determinations needed are those of total lime and total sulfide. If chlorides are added to the liquor, the determination of chloride is required, and so on. The second purpose for which the analysis may be required is to determine to what extent the various by-products of unhairing have accumulated in the liquor. This involves principally the determination of nitrogenous matter in its several states of degradation from protein to ammonia. Methods for these determinations have been evolved by the Department of Leather Research (Foundation Tanners' Council of America), University of Cincinnati, and published by Highberger and Moore (24). Methods for determining the caustic alkalinity and the alkalinity due to ammonia, to sulfides, and to sodium salts of protein decomposition products have been developed by Atkin (5) and others.

Total Lime.—Thoroughly agitate the liquor, either by plunging or by running the paddle wheel if the vats are so equipped, to bring all solid lime into suspension. Take a sample of about 1 l., preserve in a well-stoppered bottle, and mix thoroughly just before pipetting the sample for analysis.

Pipette 200 cc. of the well-shaken liquor into an Erlenmeyer flask. It is advisable to use a pipette whose tip has been broken off to give a wide orifice, the pipette being then recalibrated. Add several drops of phenolphthalein indicator. Titrate with normal sulfuric acid, added dropwise as rapidly as possible, swirling the solution vigorously to avoid local excess of acid, until the pink color disappears in streaks. Then retard the rate of addition somewhat, but continue to add acid steadily until the pink color disappears entirely and does not return for 1 or 2 sec. Note the reading, and ignore the return of color. Calculate and report total lime in pounds per gallon. It is convenient to calculate not only the weight of 100-per cent calcium oxide or hydroxide but also the corresponding weight of the particular commercial lime used in the vat.

$$\text{Lb. CaO} = 0.001168 \times \text{cc. 1-N}$$

$$\text{Lb. Ca(OH)}_2 = \text{Lb. CaO} \times 1.321$$

$$\text{Lb. commercial lime} = \frac{\text{Lb. CaO (or Ca(OH)}_2\text{)}}{\text{per cent available CaO (or Ca(OH)}_2\text{) in lime}}$$

By this procedure, not only the lime in solution but also the suspended lime, available as a reserve, is determined. Any sulfides and ammonia present are partly neutralized during the titration, but these are generally present in small amounts compared to lime. The method should not be used on liquors containing large quantities of sulfides.

Total Caustic Alkalinity (Method of Atkin and Atkin) (5).—Filter a portion of the liquor through folded filter paper, returning the filtrate until it

comes through clear. Pipette 25 cc. into each of two 50-cc. colorimeter tubes. To one of the tubes add 25 cc. of distilled water. Place 50 cc. of distilled water in a third tube, and 50 cc. of a standard buffer solution of $\text{pH} = 10.0$ in a fourth tube. This solution is made by mixing 38 cc. of tenth-normal ammonium hydroxide and 12 cc. of tenth-normal ammonium chloride. Place the tube containing lime liquor plus water behind the standard buffer in one side of a comparator, and place the tube containing water behind the undiluted lime liquor in the other side. Add 10 drops of a 0.2-per cent solution of thymolphthalein to the standard buffer solution and to the undiluted lime liquor.

Add tenth-normal hydrochloric acid to the undiluted lime liquor, slowly, with stirring, until the color nearly matches that of the standard buffer solution. Then dilute to a volume of nearly 50 cc. with distilled water, and continue the titration until an exact color match is obtained.

According to Atkin and Atkin, at $\text{pH} = 10.0$, calcium- and sodium hydroxide are neutralized practically completely, and ammonium hydroxide is neutralized to the extent of about 24 per cent. The titration will include sodium hydroxide formed by the hydrolysis of sulfides to sulphydrates, which is practically complete even at the pH value of saturated calcium hydroxide solution but does not include that which would be formed by the further hydrolysis of sulphydrate to hydrogen sulfide and sodium hydroxide, since this reaction proceeds only to a negligible extent at $\text{pH} = 10.0$.

A simpler method of determining caustic alkalinity is by calculation from the determination of pH value. The method given above is, however, useful in case a potentiometer is not available and also in solutions containing so much sulfide that the electrometric determination of pH value is practically impossible.

Determine free ammonia as directed below. Calculate and report caustic alkalinity in terms of normality.

where A is number of cubic centimeter of tenth-normal hydrochloric acid required for 25 cc. of lime liquor and B is number of cubic centimeter of tenth-normal hydrochloric acid required for titration of ammonia distilled from 25 cc. of lime liquor.

Volatile Nitrogen as Ammonia (Method of Thompson and Suzuki) (35).—Free ammonia is determined by distillation into an excess of standard acid. In order to prevent the decomposition of other protein decomposition products with the formation of more ammonia during the course of the determination, it is necessary to distil under reduced pressure at a temperature not exceeding 60°C . Volatile amines are distilled and titrated with ammonia, but the amount of these substances present is usually very small compared to the amount of ammonia. A method for separating amines from ammonia, adapted from Highberger and Moore (24), is given below.

Assemble the apparatus as shown in Fig. 65. *A* is a wash bottle containing dilute sulfuric acid to remove traces of ammonia from the incoming air, connected to the distilling flask by a line carrying a stopcock *a*. *B* is a Kjeldahl flask, immersed in a water bath *C*. The tube *b* which serves to admit air extends nearly to the bottom of the flask and is drawn to a point. *D* is a connecting bulb, *E* a water-cooled condenser, and *F* an Erlenmeyer flask containing tenth-normal sulfuric acid. The condenser tube dips below the surface of the acid. The receiving flask is connected to a vacuum pump by means of a line containing a three-way stopcock *f*. During distillation, the cock is set as shown in the diagram; when it is desired to interrupt the distillation, the cock is turned counterclockwise so as to admit air to the pump while preventing the acid in the receiver from being sucked back.

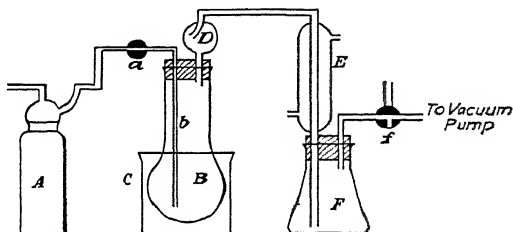


FIG. 65.—Apparatus for determination of ammonia by vacuum distillation.

Place from 50 to 250 cc. of lime liquor, depending upon the amount of ammonia expected, in the distillation flask. Place 50 cc. of tenth-normal sulfuric acid in the receiver. Close *a*, and connect *F* to the pump. Heat the water in the bath to 60°C. Start the pump, and evacuate the apparatus until the liquor boils, then open *a* and admit a gentle stream of air through *b*. Maintain the temperature between 50 to 60°C. and the pressure so low that the liquor boils steadily. Continue boiling for 30 min.; then turn *f* so as to shut off the apparatus from the pump, allow the interior of the apparatus to come to atmospheric pressure, disconnect the receiving flask from the condenser, and titrate the excess acid in *F* with tenth-normal sodium hydroxide, using methyl red indicator. Reassemble the apparatus, placing 10 cc. more tenth-normal acid in the receiver, and distill for a second half hour. Repeat until the ammonia distilled in 30 min. consumes not more than 0.2 cc. of tenth-normal acid. Calculate and report the total volatile nitrogen content of the liquor as percentage of ammonia.

$$\text{Per cent volatile N (as NH}_3\text{)} = \frac{\text{cc. 0.1-N H}_2\text{SO}_4 \text{ consumed} \times 0.17}{c}$$

Volatile Amines (24).—Combine in a 500-cc. volumetric flask the titrated distillates obtained in determining total volatile nitrogen as ammonia, and dilute to not over 480 cc. Add 10 cc. of a solution containing equal parts of a 20-per cent solution of sodium hydroxide and a 30-per cent solution of sodium carbonate, and make up to the mark with water. In a brown bottle holding 700 to 800 cc., place 0.1 gm. of yellow mercuric oxide for each cubic

centimeter of tenth-normal acid consumed by the distillates in the total volatile nitrogen determination, pour in the 500 cc. of alkaline solution containing the ammonia and amines, stopper, cover with a black cloth, shake for 1 hr., and let stand overnight.

Ammonia forms an insoluble compound (unstable in the light) with yellow mercuric oxide, leaving the amines in solution. Without disturbing the mercuric oxide sediment, siphon off the supernatant liquid through a cotton plug filter, using moderate air pressure to assist filtration.

Test the filtrate for ammonia by adding to a 10-cc. portion 2 cc. of a solution containing 22.7 gm. mercuric iodide, 33.0 gm. potassium iodide, and 35.0 gm. sodium hydroxide in 1,000 cc. A red color or brown precipitate on heating indicates the presence of ammonia. If ammonia is found in the filtrate, discard the determination.

Measure 400 cc. of the filtrate into a distilling flask, and distill into a measured volume of tenth-normal sulfuric acid. Back titrate the excess acid with tenth-normal sodium hydroxide. Calculate and report percentage of volatile amines as methyl amine.

$$\text{Per cent CH}_3\text{NH}_2 = \frac{(\text{cc. } 0.1-N \text{ H}_2\text{SO}_4 - \text{cc. } 0.1-N \text{ NaOH}) \times 0.31 \times 1.25}{\text{cc. sample distilled in determination of volatile nitrogen}}$$

Ammonia.—Calculate percentage ammonia by subtracting the ammonia-equivalent of the volatile amines from the percentage of total volatile nitrogen as ammonia.

$$\text{Per cent NH}_3 = \text{Per cent volatile N as NH}_3 - (\text{Per cent CH}_3\text{NH}_2 \times 0.55)$$

Sulfide.—Pipette 25 cc. of filtered lime liquor into a beaker, and titrate with tenth-normal zinc sulfate as described under analysis of sodium sulfide. If the volume of zinc solution consumed is less than 6.5 cc., the first titration figures may be accepted as correct. If the volume of zinc solution required exceeds 6.5 cc., regard the first titration as preliminary, and repeat the determination, adding slightly less than the required volume of zinc sulfate solution, making up to 250 cc., filtering, and completing the titration on an aliquot of the filtrate. Calculate and report pounds of sulfide per gallon, in terms of whatever sulfide is used in the process.

$$\text{Lb. Na}_2\text{S (100 per cent) per gal.} = \text{cc. } 0.1-N \text{ ZnSO}_4 \times 0.00130$$

$$\text{Lb. Na}_2\text{S (60 per cent) per gal.} = \text{cc. } 0.1-N \text{ ZnSO}_4 \times 0.00217$$

$$\text{Lb. BaS (100 per cent) per gal.} = \text{cc. } 0.1-N \text{ ZnSO}_4 \times 0.00282$$

$$\text{Lb. BaS (65 per cent) per gal.} = \text{cc. } 0.1-N \text{ ZnSO}_4 \times 0.00434$$

Total Nitrogen.—Pipette 100 cc. of liquor (filtered) into a Kjeldahl flask, put in a boiling chip, add 30 cc. of concentrated sulfuric acid, and boil until the liquor darkens and most of the water is expelled. Add 10 g. of sodium sulfate or potassium sulfate, and digest over a small flame until the solution is colorless. Make alkaline, and distill the ammonia formed into an excess of standard acid, and back titrate, as described under leather analysis (Chap. II), and calculate nitrogen in pounds per gallon. If desired, the result may be calculated as collagen, though this is apt to be misleading, since most of the nitrogen in lime liquors comes from the epidermal system.

Lb. N per gal. = cc. 0.1-*N* H₂SO₄ consumed \times 0.000117
 Lb. N as collagen = lb. N \times 5.62

Chlorides.—Measure exactly 25 cc. of filtered liquor into a platinum dish. Evaporate to dryness, and heat over a burner, at a temperature not exceeding dull red heat, until all organic matter is charred. Extract the residue 5 or 6 times with hot water, filtering each portion. Make slightly acid with acetic acid. Then add a few drops of potassium chromate indicator, and titrate as directed under analysis of sodium chloride. Calculate pounds per gallon of sodium chloride or calcium chloride.

Lb. NaCl per gal. cc. 0.1-*N* AgNO₃ \times 0.001951
 Lb. CaCl₂ (100 per cent) per gal. cc. 0.1-*N* AgNO₃ \times 0.001851
 Lb. CaCl₂ (75 per cent) per gal. cc. 0.1-*N* AgNO₃ \times 0.002468

Chlorides (Modified Volhard Method) (24).—Measure with a pipette such a volume of filtered lime liquor as contains not more than 0.1 g. of sodium chloride. If the volume required is less than 10 cc., dilute 25 cc. of the liquor to exactly 250 cc., and measure a suitable aliquot. Add 25 cc. of tenth-normal silver nitrate and 10 cc. of concentrated nitric acid. Heat to a temperature just below boiling, and maintain at that temperature for 2 or 3 hr. Cool, dilute to about 100 cc., add 5 cc. of a solution containing 10 g. of pure ferric alum and 7.5 g. of nitric acid in 100 cc., and titrate the excess silver with tenth-normal potassium sulfocyanate (30). The end point is the formation of a brownish red precipitate of ferric sulfocyanate. Calculate chlorides as sodium chloride or calcium chloride, as above.

Silica, Iron, Alumina, Calcium, Magnesium, Sodium.—Evaporate to dryness such a volume of filtered lime liquor as will give about 0.5 to 1.0 g. of dry residue. Determine these constituents in the residue by the methods given under analysis of lime or calcium chloride.

pH Value.—Determine pH value by the electrometric method described in Chap. VII. It is essential that the determination be carried out in a closed vessel, protected from the carbon dioxide of the air, especially if the filtered liquor is used. If the unfiltered liquor, containing an excess of suspended lime, is employed, carbon dioxide has less effect, since any lime precipitated as carbonate is replaced by solution of the excess hydroxide. In liquors containing more than about twentieth-normal sulfide or sulfhydrate, determination of pH value by the electrometric method is impossible, so far as the authors are aware. Colorimetric determination of pH value in the presence of sulfides is unsatisfactory, because the various indicators available for alkaline solutions give erratic colors with sulfides.

Plumping Power (Method of Wilson and Gallun) (38).—This procedure measures the percentage increase in resistance to compression (*i.e.*, increase in equilibrium thickness when compressed), resulting from the treatment of skin with the unhairing liquor.

Prepare standard test pieces of skin as follows: Take a calfskin or other skin after unhairing and bating or deliming, cut out a rectangle comprising the heart of the butt, and cut this piece into pieces about 2 cm. square. Place these pieces in a large volume of a 12-per cent solution of sodium chloride, preferably in a vessel equipped with a mechanical stirrer, add methyl orange indicator, and add dilute (approximately normal) hydro-

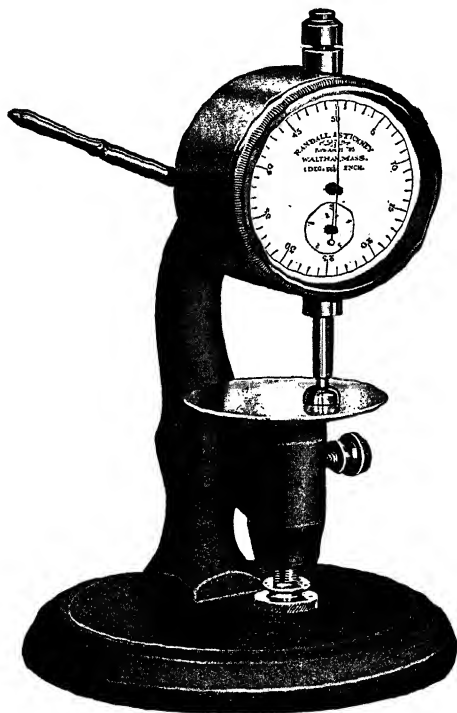


FIG. 66.—Thickness gage (Randall and Stickney Company).

chloric acid or sulfuric acid at frequent intervals until the indicator does not turn yellow on standing for several hours. Transfer the pieces to a large volume of saturated sodium bicarbonate solution, containing an excess of solid sodium bicarbonate, stir thoroughly at frequent intervals, and let stand for 24 hr. Transfer the pieces to a continuous washing apparatus, and wash, first with tap water and finally with distilled water, for 24 hr., keeping the water as cold as possible. Finally suspend the pieces in a large volume of distilled water, and keep in the ice box until needed. Pieces so prepared are good for about a week.

Determine the thickness of the test pieces before liming as follows: Remove 1 piece from the reservoir, by grasping a corner with tweezers, and blot it by laying it on a pad of filter paper. Mark the piece for identification by snipping off one, two, or three corners with a leather punch. Place the piece on the stage of the Randall and Stickney gage (Fig. 66). Let the plunger rest on the skin for exactly 3 min., and read the thickness. Determine the initial thickness of at least 3 test pieces for each liquor to be tested.

Place the test pieces, measured and marked for identification, in a bottle containing some water, and shake well to restore their original shape. Then place the pieces in about 200 cc. of the liquor in a well-stoppered bottle. Let stand at room temperature, with occasional shaking, for 4 days. Remove each piece, blot it as before, and redetermine the thickness as above. Be very careful not to handle the piece, except by grasping a corner with the tweezers.

Divide the final by the initial thickness, subtract 1.00 from the result, and report the percentage of increase in thickness of the skin, taking the average of measurements agreeing within 5 per cent.

This method has been found to give satisfactory results with both calfskin and cowhide, and there seems no reason to suppose that it will not work with any skin.

BATING AND DELIMING MATERIALS AND LIQUORS

After being unhaired by any of the usual processes involving the use of lime or other alkali, skins must be partially or wholly freed from alkali and brought into equilibrium with a solution of pH value in the neighborhood of the neutral point, which causes them to pass from a turgid to a flaccid condition (37). Frequently the accomplishment of these aims is combined with the treatment of the skins with proteolytic enzymes, which digest some of the proteins or decomposition products thereof, present in the skin after liming. The combined deliming-enzyme digestion process is known as bating.

pH regulation, deliming, and falling usually are accomplished by agitating the skins in a solution of ammonium salts. Disodium phosphate and other mildly alkaline buffer salts are sometimes used instead of ammonium salts or added in small quantities to them. Frequently the bating operation is preceded by a partial deliming with muriatic or lactic acid. The enzyme used in bating is generally pancreatin. It is entirely possible and practical for a tanner to bate with a mixture, made on the spot, of ammonium chloride or disodium phosphate and pancreatin, but in the majority of cases the enzyme and buffer salts are purchased ready mixed as a commercial dry bate. In preparing such bates,

the enzyme is generally dissolved and its solution sprayed upon sawdust or a similar inert carrier, which is then mixed with ammonium chloride. This assures a uniform distribution of the very tiny weight of dry enzyme throughout the whole product.

Skins that are not bated are delimed with muriatic, lactic, or other acid or by treatment with a fermented bran liquor (drench) containing organic acids. Sometimes deliming is effected solely by the acids formed by fermentation in the first tan liquors.

The following sections cover the analysis of ammonium salts, pancreatin, commercial mixed bates, and bate liquors. The analysis of hydrochloric, lactic, and other acids, sodium phosphate, and other alkaline sodium salts is covered elsewhere.

AMMONIUM CHLORIDE (SAL AMMONIAC)

Ammonium chloride is used in bating and forms the major part of the most commonly used mixed bates. It is occasionally used, in conjunction with sodium carbonate, for neutralizing chrome-tanned skins during or after tanning. The analysis consists in the determination of ammonia, chloride, sulfate, non-volatile matter, insoluble matter, and water.

Water.—Dry a weighed sample at 105°C., and determine loss in weight, as described under analysis of sodium chloride.

Insoluble Matter.—Determine as directed under analysis of sodium chloride.

Ammonium Salts.—Weigh accurately about 5 g., and dissolve in exactly 1 l. The filtrate from the determination of insoluble matter may be used. Pipette exactly 50 cc. into a Kjeldahl flask, dilute to 250 cc., arrange the flask for distillation as described under determination of hide substance in leather (Chap. II), make alkaline by adding a few cubic centimeters of strong sodium hydroxide solution, and distill the liberated ammonia into exactly 50 cc. of tenth-normal sulfuric acid. Back-titrate the excess acid, and calculate percentage of ammonium ion, NH_4 .

Determine total chloride in a 50-cc. aliquot of the solution by the method given under analysis of sodium chloride.

Determine total sulfate in a 200-cc. aliquot of the solution by the method given under the analysis of sodium chloride.

If any non-volatile chloride or sulfate is present (see below), subtract the percentages of non-volatile chloride and sulfate from the percentages of total chloride and sulfate. Calculate all volatile sulfate and chloride as ammonium salts. Calculate the excess ammonium, if any, as ammonium carbonate. Report percentage of ammonium chloride, ammonium sulfate, and ammonium carbonate.

Per cent total Cl

 $\frac{\text{g. sample weighed}}{\text{g. sample weighed}}$ Per cent total SO_4 $\frac{\text{BaSO}_4 \times 205.5}{\text{g. sample weighed}}$

Per cent volatile Cl = per cent total Cl - per cent non-volatile Cl

Per cent volatile SO_4 = per cent total SO_4 - per cent non-volatile SO_4

Per cent :

 $\frac{\text{cc. 0.1-N H}_2\text{SO}_4 \times 3.606}{\text{g. sample weighed}}$ Per cent NH_4Cl = per cent volatile Cl $\times 1.509$ Per cent $(\text{NH}_4)_2\text{SO}_4$ = per cent volatile $\text{SO}_4 \times 1.376$ Per cent $(\text{NH}_4)_2\text{CO}_3$ = [per cent NH_4 - (per cent volatile $\text{SO}_4 \times 0.376$) -
per cent volatile Cl $\times 0.509$] $\times 2.66$

Non-volatile Matter.—Weigh accurately about 5 g. of ammonium chloride into a weighed platinum dish. Heat over a small flame under a hood until fumes of ammonium chloride cease to be evolved. Cool in a desiccator and weigh. Calculate and report percentage of non-volatile matter.

Analysis of Non-volatile Matter.—If the non-volatile matter found exceeds 1 per cent, analyze the residue for iron, aluminum, calcium, and magnesium, by the methods given under analysis of sodium chloride. Repeat the determination of non-volatile matter, using a sample large enough to give about 0.1 g. of residue, dissolve the residue in water, make to 250 cc., and determine non-volatile sulfate and chloride in aliquots of this solution by the methods given under analysis of sodium chloride. Determine sodium in a 1-g. sample of the salt, by the method given under the analysis of calcium chloride. In the absence of weighable amounts of insoluble matter, iron, aluminum, calcium, and magnesium, the entire non-volatile residue may be assumed to consist of sodium salts. Calculate and report percentage of iron, aluminum, calcium, and magnesium as oxides, sodium equivalent to non-volatile sulfate as sodium sulfate, and the remaining sodium as chloride.

Only in very exceptional circumstances will this analysis of the non-volatile residue be required.

AMMONIUM SULFATE

Ammonium sulfate is sometimes used for the same purposes as ammonium chloride. The analysis is exactly the same as that of ammonium chloride, except that a smaller aliquot is taken for the sulfate determination, and a larger one for that of chloride.

PANCREATIN

Pancreatin is the dried, ground, and sometimes defatted pancreas of the pig. Sometimes the product is mixed with wood meal or other inert substance. By far the most important determinations are those of enzyme activity toward various

substrates. Determinations of water, ash, fat, nitrogen, and carbohydrates are of importance only in determining the method of preparation employed.

Enzyme Activity.—Determine as directed in Chap. VI.

Water.—Weigh accurately about 5 g. into a weighed platinum dish. Dry overnight at 105°C., cool in a desiccator for exactly 15 min., and weigh. Replace in the oven for 1 hr., desiccate, and reweigh. Repeat to constant weight. Calculate and report percentage of water.

$$\text{Per cent H}_2\text{O} = \frac{\text{g. H}_2\text{O} \times 100}{\text{g. sample}}$$

Ash.—Ignite the residue from the determination of water, preferably in a muffle furnace, at dull red heat, until the mass is thoroughly carbonized. Let cool. Extract the mass about 6 times with hot water, filtering through rapid paper. Preserve the filtrate. Return the paper to the dish, and ignite at bright red heat until all carbon is consumed. Evaporate the filtered water extract to a convenient bulk, transfer the solution to the dish, evaporate to dryness on the water bath, and dry at about 120°C. Cool in a desiccator, and weigh. Calculate and report percentage of ash.

Analysis of Ash.—In the ash of one sample of pancreatin, determine sodium carbonate, iron and aluminum, calcium, and magnesium, and in the ash of a second sample, determine sulfate and chloride as directed under analysis of ash of tan liquors (Chap. IX). Calculate and report percentage of iron and aluminum, calcium, and magnesium, all as oxides; sodium carbonate; chloride as chlorine and sulfate as sulfur trioxide.

Nitrogen.—Weigh accurately about 0.5 g., and determine by the Kjeldahl method, as described under analysis of leather (Chap. II). Calculate and report percentage of nitrogen.

Fat.—Weigh accurately about 5 g. into an extraction cartridge, plug the open end well with cotton, and extract with chloroform in a Soxhlett apparatus for 8 hr. Filter the extract into a weighed crystallizing dish, wash the receiving flask and filter several times with small quantities of chloroform, and let the chloroform evaporate at room temperature. (*Alternate Procedure.*—Weigh the receiving flask before starting the extraction, and distill as much of the chloroform as possible from a water bath. If this procedure is followed, care must be taken to see that the chloroform solution obtained is clear.) Heat the dish and residue at 105°C. for 20 min., cool in a desiccator, and weigh. Repeat till the loss on heating 20 min. does not exceed 5 mg. Calculate and report percentage of fat.

$$\text{Per cent fat} = \frac{\text{fat} \times 1}{\text{g. sample weighed}}$$

Matter Insoluble in Water.—Weigh accurately about 2 g., and dissolve in about 100 cc. of water, stirring well to break up any lumps that may form. Dry a quantitative filter paper, folded in eighths, for several hours at 105°C., place quickly in a stoppered weighing bottle, cool, and weigh. Filter the pancreatin solution through the weighed filter paper, transfer all insoluble

matter to the paper, and wash ten times with hot water. Dry the paper and residue in a weighing bottle with stopper removed at 105°C. for several hours. Insert the stopper, cool, and weigh. Calculate and report percentage of matter insoluble in water.

$$\text{Per cent matter insoluble in water} = \frac{\text{g. insoluble matter} \times 100}{\text{g. sample weighed}}$$

Ash of Insoluble Matter.—Ignite the paper and insoluble matter at dull red heat, preferably in a muffle furnace, until all carbon is consumed. Cool in a desiccator and weigh. Calculate and report percentage of ash of insoluble matter. Calculate percentage of organic insoluble matter by difference.

$$\text{Per cent ash of insoluble matter} = \frac{\text{g. ash} \times 100}{\text{g. sample weighed for insoluble matter}}$$

$$\text{Per cent organic insoluble matter} = \text{per cent insoluble matter} - \text{per cent ash of insoluble matter}$$

MIXED DRY BATES¹

The analysis of mixed dry bates includes the determination of the mineral constituents, of insoluble organic matter (filler), and of enzyme activity. The determinations made will depend upon the nature of the inorganic salts. The following methods are applicable to the commercial bates now in most common use.

Insoluble Matter.—Prepare a Gooch crucible, dry at 105°C., and weigh. Weigh accurately about 5 g. of bate, and dissolve in about 200 cc. of water, stir well, and filter through the Gooch. Wash the residue about 10 times with hot water. Transfer the filtrate to a 1-l. volumetric flask for use in later determinations. Dry the crucible and residue at 105°C. for several hours, cool in a desiccator, and weigh. Calculate percentage of insoluble matter.

Insoluble Ash and Insoluble Organic Matter.—Ignite the crucible and insoluble residue at dull red heat until all carbon is consumed. Cool in a desiccator and weigh. Take loss in weight as insoluble organic matter. Calculate and report as percentage. The nature of this organic insoluble matter can usually be ascertained by examining some of the insoluble matter with a hand lens. Take the incombustible residue as ash of insoluble matter, and calculate in percentage.

$$\text{Per cent organic insoluble matter} = \text{per cent insoluble matter} - \text{per cent ash of insoluble matter}$$

$$\text{Per cent ash of insoluble matter} = \frac{\text{g. ash} \times 100}{\text{g. sample weighed for insoluble matter}}$$

¹ See references, Chap. VI.

Ammonium Salts.—Make up the filtrate from insoluble matter to 1 l. Determine ammonium salts, sulfates, and chlorides in aliquots of this solution, as directed under analysis of ammonium chloride. Calculate as directed under ammonium chloride.

Non-volatile Matter.—Determine as directed under ammonium chloride.

Analysis of Non-volatile Matter.—If the non-volatile matter found exceeds 0.5 per cent, analyze it for iron and aluminum, calcium, magnesium, sulfate, chloride, and carbonate, as directed under analysis of ammonium chloride. In addition, test for and determine phosphates.

Phosphate.—Determine in an aliquot of the filtered solution of the bate by the methods given under analysis of sodium phosphate (Chap. X).

Enzyme Activity.—Determine the proteolytic activity of the bate, preferably with keratose as substrate, otherwise with casein, as directed in Chap. VI.

pH Value of a 1-Per Cent Solution.—Weigh exactly 1 g. of the bate, dissolve in 100 cc. of water, and filter. Determine the pH value of the filtrate as described in Chap. VII. The colorimetric method gives sufficiently accurate results for this determination.

Water.—Determine as directed for ammonium chloride.

USED BATE LIQUORS¹

A used bate liquor contains some of the ammonium salts added in the dry bate (assuming the bate to be of the common ammonium chloride-pancreatin type) and also other nitrogen compounds derived from the skins. Considerable calcium accumulates from the interaction of ammonium chloride and lime. Bacteria are always present in enormous numbers. The most important characteristic of a used bate liquor is its pH value. The total nitrogen content is of little significance, unless the determination is so conducted as to distinguish between ammonium salts, deliberately added, and nitrogen derived from partial digestion of the skin proteins or their decomposition products. The latter quantity is not, as some have assumed, a measure of "dissolved hide substance," since most of the degraded protein nitrogen found in old bates comes from the decomposition products, chiefly keratoses, left in the skin after liming, the removal of which is an important function of the enzyme contained in the bate.

pH Value.—Filter a portion of the liquor through folded paper, returning the filtrate until no improvement in clarity is seen to take place. Determine the pH value of the filtrate, either by the electrometric method or by colorimetric method (Chap. VII). If the colorimetric method is used, fill 2 tubes with the bate liquor and place one of them in front of the standard

¹ See references, Chap. VI.

tube in the comparator. Place a tube containing distilled water in front of the second bate-liquor tube, to which the indicator is added. This procedure compensates for the slight cloudiness of the bate liquor. The indicators required for determining the pH value of a used bate liquor, if, as is generally the case, its pH value is between 7 and 9, are phenol red, cresol red, and thymol blue.

Bacterial Count.—Determine as directed in Chap. V. The bacterial counts of old bate liquors examined by the authors have ranged between 100,000,000 and 1,000,000,000 organisms per cubic centimeter, and this high count must be taken into consideration in planning the dilutions.

Total Nitrogen.—Pipette 25 cc. of filtered liquor into a Kjeldahl flask, and determine as directed under the analysis of lime liquors. Calculate and report percentage of total nitrogen.

$$\text{Per cent :} \quad \frac{\text{cc. 0.1-}N \text{ H}_2\text{SO}_4 \text{ consumed} \times 0.14}{\text{cc. sample}}$$

Ammonium Salts.—Determine as directed under analysis of lime liquors. In very old liquors, it sometimes is impossible to reach a definite end point in the distillation of ammonia, since even when the distillation is carried out under reduced pressure at 60°C., the decomposition of the partly digested nitrogenous matter causes ammonia to be evolved continually in measurable amounts. Consider the determination complete when the quantity of ammonia evolved and titrated in successive ½-hr. distillation periods becomes practically constant. Calculate and report percentage of ammonia.

$$\text{Per cent NH}_3 = \frac{\text{cc. 0.1-}N \text{ H}_2\text{SO}_4 \text{ consumed} \times 0.17}{\text{cc. sample}}$$

Chlorides.—Determine as directed under analysis of lime liquors. Calculate and report percentage of chlorine.

$$\text{Per cent Cl} \quad \frac{\text{cc. 0.1-}N \times 0.3546}{\text{cc. sample}}$$

Sulfate.—Pipette 50 cc. of filtered liquor into a beaker, dilute to about 200 cc., and add about 1 g. of sodium peroxide, in small increments to destroy organic matter. Boil for about 20 min., acidify with hydrochloric acid, and add about 10 cc. of 10-per cent barium chloride solution, drop by drop with stirring. Let the precipitate settle for several hours, filter through Whatman No. 44 paper or its equivalent, and wash free from chlorides. Ignite in a weighed crucible, beginning at a low temperature and ending at the highest temperature attainable with an ordinary Bunsen burner, allowing free access of air to the contents of the crucible. Cool in a desiccator, and weigh. Calculate and report percentage of sulfate as sulfur trioxide.

$$\text{Per cent SO}_3 \quad \frac{\text{g. BaSO}_4 \times 0.3}{\text{cc. liquor taken}}$$

Calcium.—Pipette 50 cc. of filtered liquor, and determine calcium as directed under analysis of lime liquors. Calculate and report percentage of calcium as calcium chloride.

$$\text{Per cent CaCl}_2 = \frac{\text{g. CaO} \times 1.98}{50}$$

DRENCHES

The important characteristics of a drench are its pH value, total titratable acid content, and volatile acid content.

pH Value.—Filter, pipette exactly 50 cc. of the filtrate, and determine pH value by the electrometric method, as described in Chap. VII.

Total Acid as Lactic Acid.—Titrate the sample used for determining pH value to pH = 7, as described in Chap. VII, using normal sodium hydroxide. Calculate and report total acid as lactic acid. (*Alternate Procedure.*—Pipette 50 cc. of filtered liquor, add a few drops of phenolphthalein, and titrate with tenth-normal sodium hydroxide to the production of a permanent pink color.)

$$\text{Per cent total acid (as lactic)} = \text{cc. 1-N NaOH} \times 0.1801$$

Volatile Acid.—Assemble an apparatus consisting of a 500-cc. flask, closed with a 2-hole stopper one opening of which connects by means of a gooseneck tube to a water-cooled, vertical condenser; and the other admits a glass tube, extending nearly to the bottom of the flask, which serves as a steam injector. Place several hundred cubic centimeters of recently boiled water in a 1-l. flask, which serves as a steam generator. Close this flask with a 2-hole stopper, carrying an angle tube that can be connected to the distilling flask and a vertical tube extending nearly to the bottom of the flask, which serves as a pressure regulator. Pipette 50 cc. of filtered liquor into the distillation flask. Heat nearly to boiling. Heat the water in the steam generator to boiling, connect to the distillation flask, and pass steam through the liquor. Collect 50 cc. of the distillate, add 2 drops of phenolphthalein indicator, and titrate with tenth-normal sodium hydroxide till a pink color is produced that is permanent for about 10 sec. Continue the distillation, titrating each successive fraction of 15 cc. of distillate, until this quantity requires not more than 0.1 cc. of tenth-normal alkali. Calculate and report percentage of volatile acid as acetic acid.

$$\text{Per cent acetic acid} = \text{cc. 0.1-N NaOH} \times 0.012$$

References

1. AMERICAN PUBLIC HEALTH ASSOCIATION: "Standard Methods of Water Analysis," 6th ed., 1925.
2. AMERICAN SOCIETY FOR TESTING MATERIALS: Standard Methods of Chemical Analysis of Lime Stone, Quicklime, and Hydrated Lime, A. S. T. M. Standards, Supplement, 1929. C 25-29.
3. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS: "Methods of Analysis," 2d ed. Washington, 1925.
4. ATKIN, W. R., Committee on Limeyard Control: V, Analysis of Commercial Sodium Sulfide, *J. Soc. Leather Trades Chem.*, 6, 239, 1922; abstracted in *J. Am. Leather Chem. Assoc.*, 17, 649, 1922.

5. ATKIN, W. R., and J. ATKIN, Committee on Limeyard Control: IV, Caustic Alkalinity of Lime Liquors, *J. Soc. Leather Trades Chem.*, **4**, 236, 1920; *J. Am. Leather Chem. Assoc.*, **16**, 85-93, 1921.
6. ATKIN, W. R. and W. E. PALMER, Committee on Limeyard Control: II, Analyses of Lime Liquors, *J. Soc. Leather Trades Chem.*, **4**, 111, 1920; *J. Am. Leather Chem. Assoc.*, **15**, 620, 1920.
7. ATKIN, W. R., J. C. WATSON, and P. E. KNOWLES, Committee on Limeyard Control: VII, Reaction between Lime and Red Arsenic, *J. Soc. Leather Trades Chem.*, **8**, 471, 1924.
8. BENNETT, H. G.: Analysis of Tannery Lime Liquors, *Collegium*, London ed., 258-266, 313-322, 329-335, 1915; *J. Am. Leather Chem. Assoc.*, **11**, 98-130, 1916.
9. BENNETT, H. G.: Estimation of Sulfide in Lime Liquors, *Collegium*, London ed., 219-223, 1916; *J. Soc. Leather Trades Chem.*, **1**, 3-8, 1917; *J. Am. Leather Chem. Assoc.*, **11**, 585-591, 1916, **12**, 626-632, 1917.
10. BERNARD, W.: Analysis of Technical Hydrosulfide Liquors, *Zeit. Angew. Chem.*, 289, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 38, 1926.
11. BERNARD, W.: Analysis of Technical Sodium Hydrosulfide, *Cuir tech.*, **15**, 490-491, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 162, 1927.
12. BLUNT, T. P.: Analysis of Commercial Lime, *Analyst*, **51**, 625, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 113, 1927.
13. BAILAR, J. C.: Analysis of Lime, *Ind. Eng. Chem.*, **18**, 389, 1926.
14. BURTON, D., Committee on Limeyard Control: I, Analysis of Lime Liquors, *J. Soc. Leather Trades Chem.*, **4**, 32, 1920; *J. Am. Leather Chem. Assoc.*, **15**, 308-323, 1920.
15. BURTON, D., and J. K. HASLAM: Notes on Water Analysis, *J. Soc. Chem. Ind.*, **46**, 111, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 652, 1927.
16. CALCOTT, W. S., F. L. ENGLISH, and F. B. DOWNING: Analysis of Sodium Sulfide, *Ind. Eng. Chem.*, **17**, 176, 1925.
17. CANTONI, O.: Analysis of Sodium Sulfide, *Gior. Chim. Ind. Appl.*, **8**, 316, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 166, 1927.
18. ENNA, F. G. A.: Determination of Alkaline Sulfides in Lime Liquors, *J. Soc. Leather Trades Chem.*, **5**, 131, 1921.
19. EVANS, J. V. R., et. al.: Analysis of Materials in Connection with Beamhouse Procedure, *J. Am. Leather Chem. Assoc.*, **11**, 221-225, 1916.
20. FOOT, H. W., and W. M. BRADLEY: Determination of Calcium by Conversion of Oxalate to Carbonate, *J. Am. Chem. Soc.*, **48**, 676, 1926.
21. GRIFFIN, R. C.: "Technical Methods of Analysis," McGraw-Hill Book Company, Inc., New York, 1921.
22. HASLAM, R. T., F. W. ADAMS, and R. H. KEAN: Rate of Solution and Availability of Commercial Lime, *Ind. Eng. Chem.*, **18**, 19, 1926.
23. HAYES, H.: Sodium Sulfide in Lime Liquors, *J. Soc. Leather Trades Chem.*, **2**, 258, 1918; abstracted in *J. Am. Leather Chem. Assoc.*, **14**, 27, 1919.
24. HIGHBERGER, J. H., and E. K. MOORE: Methods for the Analysis of Beamhouse Liquors, *J. Am. Leather Chem. Assoc.*, **24**, 68-76, 1929.
25. KUBELKA, V.: Lime Liquor Analysis, *Gerber*, 52, 1928.

26. McCANDLISH, D., and J. A. WILSON: Determination of Alkaline Sulfides, *J. Am. Leather Chem. Assoc.*, **11**, 598-602, 1916; *ibid.*, **12**, 633-634, 1917.
27. PICKLES, J. E., Committee on Limeyard Control: III, Estimation of Sulfide, *J. Soc. Leather Trades Chem.*, **4**, 231, 1920; abstracted in *J. Am. Leather Chem. Assoc.*, **15**, 673, 1920.
28. PROCTER, H. R.: "Leather Industries Laboratory Book," 2d ed., E. & F. N. Spon, London and New York, 1908; "Leather Chemist's Pocket-book," E. & F. N. Spon, London and New York, 1912.
29. ROGERS, J. S.: Composition of Commercial Limes, *Ind. Eng. Chem.*, **19**, 1157, 1927; Fineness and Available Lime Content of Chemical Quicklime, *ibid.* **20**, 1,355, 1928.
30. SCOTT, W. W., ed.: "Standard Methods of Chemical Analysis," 4th ed. revised, 2 vols., D. Van Nostrand Company, Inc., New York, 1927.
31. SHAW, W. M., W. H. MACINTYRE, and J. E. UNDERWOOD: Determination of Caustic Value of Lime, *Ind. Eng. Chem.*, **20**, 312, 315, 1928.
32. STIASNY, E., ed.: "Gerbereichemisches Taschenbuch," 2d ed., Theodor Steinkopff, Dresden and Leipzig, 1929.
33. THOMPSON, F. C.: First General Report of the Limeyard Control Committee: Lime Liquors, *J. Soc. Leather Trades Chem.*, **7**, 394, 1923; *J. Am. Leather Chem. Assoc.*, **18**, 662, 1923.
34. THOMPSON, F. C., and W. R. ATKIN: Analysis of Lime Liquors, *J. Soc. Leather Trades Chem.*, **4**, 15, 1920; abstracted in *J. Am. Leather Chem. Assoc.*, **15**, 245, 1920.
35. THOMPSON, F. C., and K. SUZUKI: Determination of Ammonia in Used Lime Liquors, *J. Soc. Leather Trades Chem.*, **1**, 140, 1917; abstracted in *J. Am. Leather Chem. Assoc.*, **13**, 132, 1918.
36. VEITCH, F. P., and T. D. JARRELL: Determination of Available Calcium Oxide in Lime Used for Unhairing Hides, *J. Am. Leather Chem. Assoc.*, **16**, 438-444, 1921.
37. WILSON, J. A.: "The Chemistry of Leather Manufacture," 2d ed., vol. I, A. C. S. Mon. Ser., The Chemical Catalog Company, Inc., New York, 1928.
38. WILSON, J. A., and A. F. GALLUN, JR.: Direct Measurement of Plumping Power of Tan Liquors, *Ind. Eng. Chem.*, **15**, 376, 1923.
39. WYLER, J. A.: Analysis of Sodium Sulfide Crystals, *Color Trade J.*, **9**, 159, 1921; abstracted in *J. Am. Leather Chem. Assoc.*, **17**, 131, 1922.

CHAPTER IX

VEGETABLE TANNING MATERIALS

The analysis of vegetable tanning materials, particularly the determination of the tannin content thereof, has received more study than any other phase of leather chemistry. The determination of tannin possesses a twofold importance: first, in enabling the tanner to control the strength of the liquors in which the skins are tanned and, second, in providing a basis for the evaluation of the materials that the tanner purchases. With the disappearance of the forests, near which most tanneries originally were located, most tanners were forced to give up the practice of leaching tannin themselves from barks and woods and to depend upon extracts, prepared at a few points located near to the remaining sources of supply. Thus there has grown up the tannin-extract business, producing annually many millions of dollars worth of tanning materials. The amount of money spent for vegetable tanning materials by even a small tannery made it imperative that standards be set up by means of which this merchandise could be evaluated. This necessity was rendered more acute by the complicated nature of all natural tanning materials. In extracting a bark, wood, or other tannin-containing substance, not only is the true tannin dissolved but also any other soluble substances that the plant contains. While these soluble non-tannins play an important role in the tanning process, it was obviously necessary to distinguish between them and the true tannins, if only to prevent unscrupulous manufacturers from adulterating their extracts with soluble organic matter having no tanning value at all. Numerous methods for determining tannin in an extract have been proposed, but one method has now been accepted practically universally. This is the well-known "hide powder method," in which a solution of the tan liquor is brought in contact with shredded skin, then filtered, and the soluble material which has not combined with or been absorbed by the hide weighed as "non-tannin," tannin thus being determined by difference. Due to geographical and

political reasons, slightly different forms of this method were used in the United States (1) in the Germanic and Scandinavian countries, and in the countries at war with Germany in 1914 to 1918 (38), until 1927, when a compromise international method was adopted. At this writing, both the new international method and the previously existing official method of the A. L. C. A. are recognized as official in the United States, but it appears that the difference in result between the two is negligible (61, 65, 77).

The official method was criticized by Wilson and Kern (105) on the ground (among others) that much of the material taken up by hide powder and hence reported as tannin is not really combined with the hide, since it is incapable of precipitating gelatin and is readily displaced from the hide powder by washing. They devised and published the Wilson-Kern method (90, 105), which in essence differs from the official method in that the tanned hide powder is washed free from all soluble matter, dried, and weighed, tannin thus being determined directly. The percentage of tannin found in a given tannin extract by the Wilson-Kern method is very much less than the percentage found by the official method—from a third to two-thirds as much, depending upon the material. Largely on account of this drastic difference in results, the Wilson-Kern method has never received serious consideration as a substitute for the existing official method. From the standpoint of price fixing, the only effect of such a substitution would be to increase the price charge per unit of tannin, with resulting confusion and inconvenience to all concerned. That the tannin content of extracts, as determined by the official method, is a purely arbitrary quantity is not a serious objection to its use for price-fixing purposes, so long as the quantities found in a given extract by different analysts are the same. This condition the official method fulfills, provided the method as adopted is followed scrupulously in every detail. From the standpoint of the scientific investigation of the tanning process, or the control of the tan yard, the Wilson-Kern method is, in the authors' judgment, very much more useful.¹

¹ Recent work by Page indicates that, in the case of wattle solutions, the tannin content found by the A. L. C. A. method agrees well with the sum of fixed tannin and "fixed water soluble matter" found in hide powder tanned in these solutions, so long as the exhausted liquor does not respond

In addition to the determination of insoluble matter, tannin, and soluble non-tannin, the analysis of tanning materials should include a number of determinations, not included in the official methods, which are valuable in safeguarding the tannery against the introduction of undesirable materials into the tan liquors. These determinations include those of ash (soluble and insoluble), the composition of the ash, glucose, sulfates, chlorides, and the pH value of a solution of definite strength.

The analysis of used tan liquors is, in general, very much like that of tanning extracts. The most important determinations are those of pH value, tannin and non-tannin, ash, and specific constituents of the ash.

METHODS OF THE A. L. C. A. (1,102)

PROVISIONAL METHOD FOR SAMPLING TANNING MATERIALS (3)

General.—All tanning materials contain moisture in different proportions, depending on the nature of the material and also on climatic conditions, so that sampling must be carried out as quickly as is consistent with thoroughness in order to avoid change in moisture.

Immediately after taking samples, they shall be put into clean, dry glass bottles, well corked, sealed, and labeled.

Four samples shall, in general, be taken: one each for the buyer, the seller, the independent analyst, and the fourth as reserve in case one of the samples is lost or damaged.

All extracts and crude tanning materials shall be sampled as nearly as possible at the time of weighing.

1. Number of Package to Be Sampled.—The number of packages to be sampled out of any given lot of tanning material composed of solid extract, powdered extract, pasty extract, or crude or manufactured tanning materials in bales, boxes, bags, or similar packages shall be shown in the following table:

Number of packages in lot, inclusive	Number of packages to be sampled	Number of packages in lot, inclusive	Number of packages to be sampled
200 to 250	4	3,151 to 3,200	53
251 to 300	5	3,201 to 3,300	54
301 to 350	6	3,301 to 3,400	55
351 to 400	7	3,401 to 3,450	56
401 to 450	8	3,451 to 3,500	57
451 to 500	9	3,501 to 3,600	58
501 to 550	10	3,601 to 3,700	59
551 to 600	11	3,701 to 3,750	60
601 to 650	12	3,751 to 3,800	61
651 to 700	13	3,801 to 3,900	62

to the gelatin-salt test. The *ratio* of fixed tannin to fixed water solubles varies with the concentration of wattle, but their sum is nearly independent of concentration. However, Henrich has since shown that this is not true for oak bark extract.

Number of packages in lot, inclusive	Number of packages to be sampled	Number of packages in lot, inclusive	Number of packages to be sampled
701 to 800	14	3,901 to 4,000	63
801 to 850	15	4,001 to 4,100	64
851 to 900	16	4,101 to 4,200	65
901 to 950	17	4,201 to 4,250	66
951 to 1,000	18	4,251 to 4,300	67
1,001 to 1,050	19	4,301 to 4,400	68
1,051 to 1,100	20	4,401 to 4,500	69
1,101 to 1,150	21	4,501 to 4,600	70
1,151 to 1,200	22	4,601 to 4,700	71
1,201 to 1,300	23	4,701 to 4,800	72
1,301 to 1,350	24	4,801 to 4,900	73
1,351 to 1,400	25	4,901 to 5,000	74
1,401 to 1,450	26	5,001 to 5,100	75
1,451 to 1,500	27	5,101 to 5,200	76
1,501 to 1,600	28	5,201 to 5,300	77
1,601 to 1,650	29	5,301 to 5,400	78
1,651 to 1,700	30	5,401 to 5,500	79
1,701 to 1,750	31	5,501 to 5,600	80
1,751 to 1,800	32	5,601 to 5,750	81
1,801 to 1,900	33	5,751 to 5,900	82
1,901 to 1,950	34	5,901 to 6,000	83
1,951 to 2,000	35	6,001 to 6,100	84
2,001 to 2,050	36	6,101 to 6,250	85
2,051 to 2,100	37	6,251 to 6,400	86
2,101 to 2,200	38	6,401 to 6,550	87
2,201 to 2,250	39	6,551 to 6,700	88
2,251 to 2,300	40	6,701 to 6,800	89
2,301 to 2,400	41	6,801 to 7,000	90
2,401 to 2,450	42	7,001 to 7,200	91
2,451 to 2,500	43	7,201 to 7,350	92
2,501 to 2,600	44	7,351 to 7,500	93
2,601 to 2,650	45	7,501 to 7,750	94
2,651 to 2,700	46	7,751 to 8,000	95
2,701 to 2,800	47	8,001 to 8,250	96
2,801 to 2,850	48	8,251 to 8,500	97
2,851 to 2,900	49	8,501 to 9,000	98
2,901 to 3,000	50	9,001 to 9,500	99
3,001 to 3,100	51	9,501 to 10,000	100
3,101 to 3,150	52		

For a less number of packages than 200, three samples shall be taken. For every 1,000 packages in excess of 10,000, one sample shall be taken.

2. Method of Taking Samples of Solid Extract. *Quebracho, Mangrove, Wattle, Etc.*—The calculated number of packages shall be selected from as uniformly distributed parts of the consignment as possible. After removal of the exterior covering of the package, a V-shaped wedge of from 4 to 5 in. on the surface of the flat side of the package and as near the middle as possible shall be cut to the center of the bag, as shown in the following illustration (Fig. 67).

The dry exterior portion of the sample shall not be removed by brushing or otherwise. Immediately on taking a sample it shall be wrapped in canvas to prevent exposure to air. This canvas shall be of 11-oz. weight. The total number of samples shall be broken up as soon as possible after taking, without undue exposure to air, until it will pass through a sieve of 1-in. mesh and then reduced to the required bulk by mixing and quartering.

The entire sample thoroughly mixed is spread out on canvas cloth and quartered, as shown in Fig. 68. Opposite quarters *a* and *b* are entirely removed with a small flat scoop, using care that all fine powdery material in any of the quarters taken is removed, mixed, spread out, quartered as in *Y* and the quarter *c* and *d* thoroughly mixed and spread out and quartered as in *Z*, and each entire quarter shall be placed in a sampling jar if approximately of 6 oz. If not, the process is repeated until the weight obtained in each quarter is approximately 6 oz.

Samples shall be wrapped in paraffin paper, put in 1-pt. mason jars, sealed, and properly labeled. When preparing samples for analysis, foreign matter from the package covering shall be removed before weighing.

3. Pasty Extracts, Gambier, Etc.—Pasty extracts shall be sampled as in 1 and 2. As such extracts cannot be broken up, portions as nearly as possible representing the exterior and interior of the package shall be weighed out for analysis.

4. Powdered Extracts, Chestnut, Valonea, Etc.—Sampling shall be carried out employing an instrument similar to a large cheese or butter sampler. Three samples shall be drawn from each of the specified number packages, one from the middle, one midway between the middle and the top, and one midway between the middle and the bottom of each package. Each sample taken shall extend to as nearly the center of the package as possible. These samples shall be thoroughly mixed, reduced by quartering, put in the smallest clean, dry, glass containers, sealed, and properly labeled. Each sample shall be at least 6 oz. unless otherwise specified.

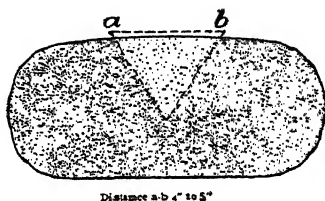


FIG. 67.—Method of sampling solid extract.

5. Bark and Wood in Sticks.—Barks and other materials in bundles shall be sampled by cutting a section about $1\frac{1}{2}$ in. long from the middle of the calculated number of bundles. A saw or strong shears are recommended for cutting. The samples shall be mixed, reduced by quartering to the desired size, which shall be not less than 2 lb., bottled, and sealed immediately.

6. Bark and Wood in Sticks or Logs (Bulk Shipment).—The calculated number of pieces set aside representing the varying sizes in the consignment shall be sawed through. The sawdust shall be well mixed by quartering; and a quantity which shall not be less than 1 lb. for each sample, bottled and sealed immediately.

7. Wood in Chips.—The chips from the chipping machine shall be taken at regular intervals and placed in a closed container to prevent loss of moisture. The sample shall be divided by quartering, and at least 1 lb. for each sample bottled and sealed immediately.

Samples are not representative when water is used to lay dust in chipping.

8. Fruits, Roots, Galls, Leaves, Etc., in Sacks or Bales.—Samples shall be drawn as in (4), using a scoop when necessary instead of the sampling instrument.

a. Valonea.—The relative proportion of cups and beards in any given lot sampled shall be taken for analysis.

Samples of at least 5 lb. shall be taken whenever possible.

9. Spent Tanning Materials.—Samples shall be taken representing the top, center, bottom, and outer portions of the leach, thoroughly mixed, quartered, and at least 2 lb. set aside for each sample.

10. Tanning Liquors.—The liquors shall be thoroughly mixed by plunging or other effective means and preserved with a suitable antiferment such as thymol, in amount of 0.03 per cent. If routine samples are taken daily, these shall be of equal size. These samples shall be mixed, placed in covered containers, and preserved with an antiferment. Samples of liquor for analysis shall be not less than 1 pt.

11. Liquid Extract. General.—Liquid extracts shall not be sampled while frozen. Samples of liquid extract prone to fermentation shall have the addition of a suitable preservative and shall be sealed immediately to prevent

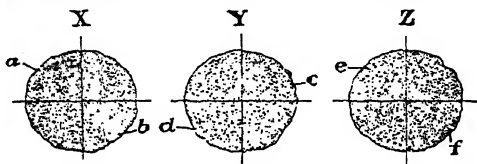


FIG. 68.—Method of quartering a sample of solid extract.

loss of moisture. A sample shall not be taken if direct steam has been used to aid the unloading of the extract.

a. In Barrels.—The number of barrels to be sampled shall be 5 per cent of the total number in the lot and shall be taken from an evenly distributed part of the total consignment. Before sampling, the contents of the barrels shall be mixed thoroughly by rolling. To assist this procedure, two copper or wooden pails of the extract shall be drawn before rolling, barrels rolled, extract returned, and the barrels again rolled. Samples of at least 1 lb. shall be taken from each barrel sampled by plunging a brass or copper tube of 1 in. diameter through the bunghole to the opposite side of the barrel, collected in one vessel, thoroughly mixed, and samples of at least 4 oz. bottled, sealed, and labeled.

b. Liquid Extract in Tank Cars.—The extract shall be sampled by inserting a clean, dry copper or brass tube very slowly into the extract through the dome of the car, then withdrawing the tube and placing the sample in a clean, dry receptacle. (The sampling tube should reach the bottom of the car and be equipped with a check valve which opens when the tube is lowered into the extract and closes when it is withdrawn.)

Two of these samples shall be taken, pointing the tube toward opposite ends of the car. The samples shall then be thoroughly mixed at once, and the required number of samples of at least 4 oz. shall be drawn and preserved in clean, dry glass containers, sealed, and labeled properly.

possible, the extract should be sampled immediately after the car is filled or immediately after delivery.

It is very important that samples be mixed and placed in stoppered glass containers promptly after taking, to prevent introduction of water into samples or loss from evaporation. The samples shall not come in contact with iron at any time during sampling.

Sampling Tube: Description.—The sampling tube shall be of 1 in. diameter brass or copper pipe of such length as to reach to the bottom of the car diagonally, and a bronze swing check valve shall be attached to the lower end with the disk opening to the top of the tube. A wire shall be fastened to the disk and run to the top of the tube for opening the check valve when the tube is lowered into the extract. The check valve shall be closed when the tube is withdrawn.

The tube shall be washed with hot water after being used and hung, with check valve up, to dry.

Sampling tubes shall be clean and dry when used.

12. A sample drawn by a member of the Association or his representative shall be accompanied by the following certificate:

I (we), the undersigned, sampler of tanning material herein described,¹ do affirm that the sample was taken in strict accordance with the provisional method of the American Leather Chemists Association for sampling tanning materials.

(Signed) SAMPLER.

13. The allowable difference in the tannin content between different laboratories on samples taken by this method of sampling shall not exceed 1½ per cent of the total tan content.

OFFICIAL METHOD FOR THE ANALYSIS OF VEGETABLE MATERIALS CONTAINING TANNIN (1, 102)

I. RAW AND SPENT MATERIALS

1. **Caution.**—Proper care must be taken to prevent any change in the water content of raw materials during the sampling and preliminary operations (see General, under Sampling).

2. **Preparation of Sample.**—The sample must be ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

a. The temperature used for drying samples of spent material for grinding must not exceed 60°C.

b. Samples of raw material too wet to be ground may be dried before grinding, as in *a*. In this case, a preliminary water determination must be made according to IV on the sample as received. If the portion of the sample taken for the water determination is in pieces too large to dry properly, it is permissible to reduce these to smaller size as rapidly and with as little loss of water as possible.

¹ A description shall have the following data whenever possible: kind of material, number of packages, distinguishing marks, number of packages sampled, weigher's lot number, any other marks descriptive of the lot sampled such as car number, order number, etc.

3. **Water Determination.**—Ten grams of the ground material shall be dried in the manner and for the period specified for evaporation and drying in extract analysis (see IV).

4. **Amount of Sample to Be Extracted.**—Such an amount of raw material shall be extracted as will give a solution containing as nearly as practicable 0.4 g. tannin to 100 cc. (not less than 0.375 or more than 0.425). Of spent materials such an amount shall be taken as will give a solution of as nearly as practicable the above concentration.

5. **Extraction.**—Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled and a container for the material to be extracted. The container shall be provided above with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted and provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber and that it may receive the percolate from the container. The condensation water from the condenser must be at approximately the boiling temperature when it comes in contact with the material to be extracted.

The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provisions must be made for preventing any of the solid particles of the material from passing into the percolate.

A. *Woods, Barks, and Spent Materials.*—Five hundred cc. of the percolate shall be collected outside in approximately 2 hr. and the extractions continued with 500 cc. for 14 hr. longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give condensation approximating 500 cc. in $1\frac{1}{2}$ hr.

B. *Materials Other than Woods, Bark, and Spent.*—Digest the material in the extractor for 1 hr. with water at room temperature, and then extract by collecting 2 l. of percolate outside in approximately 7 hr.

6. **Analysis.**—The percolate shall be heated to 80°C., cooled, made to the mark, and analyzed according to the official method of extracts.

II. ANALYSIS OF EXTRACT

7. **Amount and Dilution for Analysis.** A. *Fluid Extracts.*—Fluid extracts shall be allowed to come to room temperature, be thoroughly mixed, and such quantity weighed for analysis as will give a solution containing as nearly as possible 0.4 g. tannin to 100 cc. (not less than 0.375 nor more than 0.425). Precautions must be taken to prevent loss of moisture during weighing. Dissolve the extract by washing it into a 1-l. flask with 900 cc. of distilled water at 85°C.

Cooling.—a. The solutions prepared as above shall be cooled rapidly to 20°C. with water at a temperature of not less than 19°C., be made to the mark with water at 20°C., and the analysis proceeded with at once, or

b. The solution shall be allowed to stand overnight, the temperature of the solution not being permitted to go below 20°C., be brought to 20°C. with water at not less than 19°C., be made to the mark with water at 20°C., and the analysis proceeded with.

B. Solid and Powdered Extracts.—Such an amount of solid or powdered extract as will give a solution of the strength called for under liquid extracts shall be weighed in a beaker with proper precautions to prevent change of moisture. One hundred cubic centimeters of distilled water at 85°C. shall be added to the extract and mixture placed on the water bath, heated, and stirred until a homogeneous solution is obtained. When dissolved, the solution shall immediately be washed into a 1-l. flask with 800 cc. of distilled water at 85°C., be cooled, etc., as under A above.

NOTE.—It is permissible to make up 2- instead of 1-l. solutions, dissolving by washing into flask with 1,800 cc. water at 85°C. in case of fluid extracts and 1,700 cc. water at 85°C. in case of solid or powdered extracts.

8. Total Solids.—Thoroughly mix the solutions; pipette 100 cc. into tared dish, evaporate, and dry as directed under Evaporation and Drying (see IV).

9. Water.—The water content is shown by the difference between 100 per cent and the total solids.

10. Soluble Solids.—S. & S. No. 590 or Munktel's No. 1F, 15 cm. single, pleated, filter paper shall be used for the filtration.

The kaolin used shall answer the following test: Two grams kaolin digested with 200 cc. of distilled water at 20°C. for 1 hr. shall not give more than 1 mg. of soluble solids per 100 cc. and shall be neutral to phenolphthalein. To 1 g. kaolin in a beaker add sufficient solution to fill the paper, stir, and pour on paper. Return filtrate to paper when approximately 25 cc. has collected, repeating operation for 1 hr., being careful to transfer all kaolin to the paper. At the end of the hour remove solution from filter paper, disturbing the kaolin as little as possible. Bring so much as needed of the original solution to exactly 20°C., as described under 7, refill the paper with this solution, and begin to collect the filtrate for evaporating and drying so soon as it comes clear. The paper must be kept full, and the temperature of the solution on the filter must not fall below 20°C. nor rise above 25°C. during this part of the filtration. The temperature of the solution used for refilling the paper must be kept uniformly at 20°C., and the funnels and receiving vessels must be kept covered.

Pipette 100 cc. of clear filtrate into tared dish; evaporate and dry as under (IV).

11. Insolubles.—The insoluble content is shown by the difference between the total solids and the soluble solids and represents the matters insoluble in a solution of the concentration used under the temperature conditions prescribed.

12. Non-tannins.—The hide powder used for the non-tannin determination shall be of woolly texture, well delimed, and shall require between 12 and 13 cc. of tenth-normal sodium hydroxide to neutralize 10 g. of the absolutely dry powder.

a. Digest the hide powder with 10 times its weight of distilled water till thoroughly soaked. Add 3 per cent of chrom alum, $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, in 3-per cent solution calculated on the weight of the air-dry powder. Agitate frequently for several hours, and let stand overnight. Squeeze and wash (30, 52) by digesting with 4 successive

portions of distilled water, each portion equal in amount to 15 times the weight of the air-dry powder taken. Each digestion shall last for 15 min., and the hide powder shall be squeezed to approximately 75 per cent water after each digestion except the last, a press being used if necessary. The wet hide powder used for the analysis shall contain as nearly as possible 73 per cent of water, not less than 71 per cent nor more than 74 per cent. Determine the moisture in the wet hide powder by drying approximately 20 g. (see IV). To such quantity of the wet hide as represents as closely as practicable $12\frac{1}{2}$ g. (not less than 12.2 nor more than 12.8) of absolutely dry hide add 200 cc. of the original analysis solution, and shake immediately for 10 min. in some form of mechanical shaker. Squeeze immediately through linen, add 2 g. of kaolin (answering test described under 9) to the detannized solution, and filter through single folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning until clear. Pipette 100 cc. of filtrate into tared dish, evaporate, and dry as under (IV).

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Funnels and receiving vessels must be kept covered during filtration.

Flasks graduated to deliver 200 cc. are recommended for measuring the analysis solution to be detannized.

NOTE.—In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder, and calculate the quantity equal to $12\frac{1}{2}$ g. of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing as nearly as possible 73 per cent of water. Weigh the whole amount and divide by the multiple of the $12\frac{1}{2}$ g. of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

13. Tannin.—The tannin content is shown by the difference between the soluble solids and the corrected non-tannins and represents the matters absorbable by hide under the conditions of the prescribed methods.

III. ANALYSIS OF LIQUOR

14. Dilution.—Liquors shall be diluted for analysis with water at room temperature so as to give as nearly as possible 0.7 g. of solids per 100 cc. of solution. Should a liquor be of such character as not to give a proper solution with water of room temperature, it is permissible to dilute with water at 80°C. and cool rapidly as described under 7 A, a.

15. Total Solids.—To be determined as in extract analysis.

16. Soluble Solids.—To be determined as in extract analysis.

17. Insolubles.—Determined as in extract analysis.

18. Non-tannins.—To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing as nearly as possible 73 per cent water, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc., grams	Dry powder per 200 cc., grams
0.35 to 0.45	9.0 to 11.0
0.25 to 0.35	6.5 to 9.0
0.15 to 0.25	4.0 to 6.5
0.00 to 0.15	0.0 to 4.0

Solutions to be shaken for non-tannins as in extract analysis, and 100 cc. evaporated as in extract analysis.

IV. TEMPERATURE, EVAPORATION AND DRYING, DISHES

19. Temperature.—The temperature of the several portions of each solution pipetted for evaporating and drying, that is, the total solids, soluble solids, and non-tannins, must be identical at the time of pipetting.

20. Evaporation.—All evaporation and drying shall be conducted in the form of apparatus known as the "combined evaporator and dryer" at a temperature not less than 98°C. The time for evaporation and drying shall be 16 hr.

21. Dishes.—The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor more than 3 in. in diameter.

V. DETERMINATION OF TOTAL ACIDITY OF LIQUORS

22. Reagents. *a.*—One per cent solution of gelatin neutral to hematine. The addition of 25 cc. of 95-per cent alcohol per liter is recommended to prevent frothing. If the gelatin solution is alkaline, neutralize with tenth-normal acetic acid; and if acid, neutralize with normal sodium hydroxide.

b. Hematine.—A solution made by digesting hematine in cold neutral 95-per cent alcohol in the proportion of ½ g. of the former to 100 cc. of the latter.

c. Acid washed kaolin free from soluble matters.

d. Tenth-normal sodium hydroxide.

Directions.—To 25 cc. of liquor in a cylinder that can be stoppered, add 50 cc. of gelatin solution, dilute with water to 250 cc., add 15 g. of kaolin, and shake vigorously. Allow to settle for at least 15 min., remove 30 cc. of the supernatant solution, dilute with 50 cc. of water, and titrate with tenth-normal soda, using hematine solution as the indicator. Each cubic centimeter tenth-normal soda is equivalent to 0.2 per cent acid, as acetic.

VI. GENERAL

23. When materials containing sulphite-cellulose extract are analyzed, the fact that the material contains sulphite-cellulose extract shall be noted on the report.

24. The test for the presence of sulphite-cellulose in a liquor or extract shall be as follows: 5 cc. of a solution of analytical strength shall be placed in a test tube, 0.5 cc. of aniline added, and the whole well shaken; then 2 cc. of strong hydrochloric acid added, and the mixture again shaken. If at least as much precipitate remains as is obtained when a comparison solution

prepared as below is similarly treated, the material shall be held to contain sulphite-cellulose.

The comparison solution shall consist of sulphite-cellulose in the proportion of 1 part total solids to 2,000 cc. of solution and as much tanning material, similar to that being tested but known to be free from sulphite-cellulose, as will make up the solution to analytical strength. Attention is drawn to the fact that certain synthetic tannins give precipitates under the conditions of this method.

25. On public analytical work by members of this association the fact that the official method has been used shall be so stated.

INTERNATIONAL METHOD (2, 90, 102)

PROVISIONAL METHOD OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR THE ANALYSIS OF VEGETABLE MATERIALS CONTAINING TANNIN, EFFECTIVE JAN. 1, 1928

A. General Regulations

Apparatus

1. **Glassware.**—The glassware employed shall be resistant to the action of distilled water; graduated flasks and pipettes shall be carefully verified, and if necessary, regraduated. The graduation marks on the 1- and 2-l. flasks must be near the base of the neck.

2. **Desiccators.**—Desiccators shall possess a tight-fitting cover and contain sulphuric acid which shall not fall below a concentration of 85 per cent sulfuric acid (by weight). Only one dish shall be in each desiccator at any one time.

3. **Evaporating Basins.**—Evaporating basins must be shallow, flat bottomed, and not less than 7 nor more than 8.5 cm. in diameter. Glass basins must not be allowed to come in direct contact with steam; porcelain basins must be glazed outside and inside. Porcelain rings must be used on the water bath or steam oven when silver basins are employed.

4. **Apparatus for Evaporating and Drying.**—Evaporation must be carried out at 98.5 to 100°C. on:

- a. A water bath.
- b. A combined water bath-steam oven.
- c. A combined evaporator and dryer.

After evaporation, as in *a* or *b*, residues must be dried in an oven at a uniform and constant temperature of 98.5 to 100°C.

Water, steam, and electric ovens at ordinary pressure or under vacuum are permissible, but electric ovens must be so equipped that they will maintain an essentially constant temperature.

Gas-heated air ovens must not be used.

5. **Balances.**—Analytical balances, accurate to at least 0.2 mg. with 100 g. load, shall always be employed for weighing residues.

6. **Linen.**—Linen cloths are to be used for washing the chromed hide powder and for the preliminary filtration of the detannized solutions. The linen must be freed from weighting matter by boiling in several changes of distilled water.

7. Filter Paper.—The filter papers employed shall be pleated and 15 cm. in diameter; they must be used single. Any of the following papers may be used: Munktell No. IF, S. & S. No. 590, or Durieux Super.

8. Koch Extractor.—This apparatus (Fig. 69) consists of a wide-mouthed glass flask of 300 to 400 cc. capacity, which is thin walled and well annealed so that it will withstand continual heating in a water bath. The mouth of the flask is closed by a rubber stopper through which pass two glass tubes, one, through which the water enters, ending about 1 cm. below the bottom of the stopper in order to mix the inflowing cold water with the contained hot water; and the other, which is the outlet, going almost to the bottom of the flask, the end being enlarged into a funnel shape and the opening covered with silk gauze. Both tubes are bent at right angles just above the stopper and connected to rubber tubing. On the bottom of the flask is placed a layer of fine sea sand 2 cm. deep (the sand having been purified by washing with hydrochloric acid and water), and on the sand is placed the properly prepared material to be extracted. To fill the flask, the tube which reaches

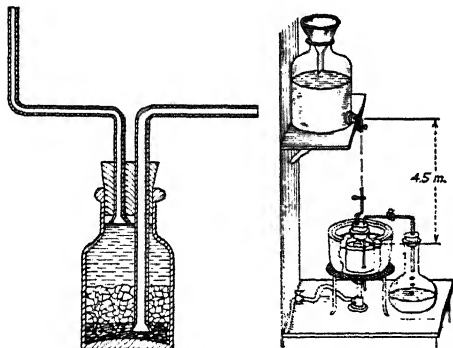


FIG. 69.—Koch extractor.

to the bottom is connected by rubber tubing to a right-angled glass tube, the free end of which dips in a beaker of water; suction is now applied to the second tube until the flask is full, when the rubber tube is then securely closed by means of a pinchcock and the apparatus placed in a water bath. The short inlet tube is next suitably connected to a 2-l. bottle standing about 150 cm. above the water bath, as shown in the accompanying diagram.

Chemicals and Reagents

9. Distilled Water.—This must comply with the following specifications:

- a. The pH must be between 5.0 and 6.0, that is, it must not yield a red color with methyl red nor a deep purple with brom cresol purple (brom cresol sulphonaphthalein).
- b. The residue, after evaporation of 100 cc., must not exceed 0.001 g.

10. Kaolin.—Kaolin must be of such quality that when 1 g. is suspended in 100 cc. of water and well shaken, the suspension will have a pH value between 4.0 and 6.0, that is, it will not give a red color with methyl orange

nor a deep purple color with brom cresol purple. When 1 g. of the kaolin is shaken with 100 cc. of tenth-normal acetic acid and the mixture filtered, the filtrate must leave less than 1 mg. of residue after evaporation and drying.

Kaolin not meeting these specifications may often be made to comply with them by digesting with hydrochloric acid and then washing with distilled water until free from soluble matter.

NOTE.—The following kinds of kaolin have been found satisfactory: LeMoor china clay and "catalpo"; but each lot must be tested and shown to conform to the above specifications.

11. Chrome Alum Solution.—Chrome alum must be crystalline and correspond in composition to the formula $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$. The solution used for chroming hide powder must be prepared at *laboratory temperature* by dissolving the alum in water in the proportion of 30 g. to 1 l. of water. The chrome alum solution must not be more than 30 days old when used.

12. Hide Powder.—The hide powder employed shall have been approved by an International Hide Powder Committee, consisting of the chairmen of the Hide Powder Committees of the A. L. C. A., the I. S. L. T. C., and the I. V. L. I. C. It must comply with the following conditions:

a. The ash content must be less than 0.3 per cent.

b. When 7 g. of the air-dry powder is suspended in 100 cc. of tenth-normal potassium chloride solution, left for 24 hr. with occasional shakings, and the mixture then filtered through filter paper, the pH of the filtrate must not be less than 5.0 nor more than 5.4.

13. Gelatin Salt Reagent.—1 gram of photographic gelatin and 10 grams of pure sodium chloride are dissolved in 100 cc. of distilled water, and the reaction adjusted to pH 4.7 approximately by adding acid or alkali; that is, the solution should give a red color with methyl red and a yellow with methyl orange. 2 cubic centimeters of toluene added to this solution will preserve it for a short time if kept to a cool place, but a freshly made solution is preferable. In the preparation of this solution the temperature must not be allowed to exceed 60°C.

Preparation of Samples for Analysis

14. Solid Tanning Materials (Woods, Barks, Fruits, Etc.).—Woods, barks, and fruits must be ground in a suitable mill until they will pass through a sieve of five wires per linear centimeter. When from the fibrous nature of a solid tanning material, it cannot be ground so as to pass entirely through the specified sieve, the finer and coarser portions must be separately weighed so as to determine the proportion of fine and coarse material in the whole amount ground. The quantity of material actually used for extraction must consist of fine and coarse material in this same proportion.

Any material giving finely divided matter (dust) on grinding must be dealt with in the same way; that is, the portion extracted must consist of dust and coarser material in the proportions existing in the whole ground sample.

Fibrous tanning materials such as leaves (sumac, etc.) and barks (oak, mimosa, mangrove, etc.) may be pounded in a mortar (preferably of copper or bronze with a heavy copper pestle) in order to break up the fibrous matter and to facilitate the penetration of the water used for extraction.

Some materials lose moisture when submitted to the grinding process, and it is advisable therefore to estimate the moisture both before and after grinding, and if any loss has taken place, the results obtained on the dried sample should be calculated back to the original moisture.

Materials yielding aqueous infusions that deposit ellagic acid, chebulinic acid, etc., such as valonia, myrabolans, etc., must be heated to 100°C. for 1 hr. before they are extracted.

15. Solid Extracts.—Solid extracts shall be ground in a porcelain or agate mortar before weighing for analysis. In case the solid extracts are of uneven moisture content and cannot be pulverized and ground, the blocks should be broken up, a portion weighed in a flat-bottomed basin, allowed to dry in an oven at 70°C. for some hours, and then be left exposed to the atmosphere of the laboratory for several hours (preferably overnight). After this partial drying, the extract is weighed and the loss of water calculated. The extract is next finely pulverized in a mortar, and a weighed portion is dried in an oven between 98.5 to 100°C. to constant weight. This new loss of moisture is added to the first for calculating the percentage of water in the original sample.

Pasty extracts, such as block gambier, should be cut up into small portions and treated in the same way.

16. Liquid Extracts.—Liquid extracts shall be thoroughly mixed so as to ensure a perfectly homogeneous sample, care being taken to include any sediment that has settled in the bottom of the container. Viscous extracts shall be heated to 45°C. on a water bath, well mixed, cooled to 18°C. (see paragraph 21), and then weighed at once. This heating must be mentioned on the report.

Preparation of Infusion

17. Such a quantity of material shall be employed as will give a solution containing as nearly as possible 4 g. per litre of tanning matter absorbable by hide powder and in any case not less than 3.75 nor more than 4.25 g. In the event of the results of an analysis showing a tannin strength outside these limits, the analysis must be repeated using the proper weight of material.

All materials for analysis shall be weighed out on an analytical balance to an accuracy of at least 0.002 g.

18. Extraction of Solid (Crude) Tanning Materials.—Solid tanning materials ground as previously described shall be extracted in a Koch extractor, using such a quantity as to give 2,000 cc. of solution of the required analytical strength (see paragraph 17). The material must be soaked in cold distilled water in the extractor (see paragraph 8) for not less than 12 nor more than 18 hr. (e.g., overnight) before commencing extraction.

At the end of this time the infusion must be drawn off and the extraction be continued at such uniform speed that the required 2 l. will be obtained in 4 hr. When the first 150 cc. have been collected, the temperature of the water bath must be raised to 50°C., and at this temperature an additional 750 cc. collected. The temperature must then be raised rapidly to boiling and the further quantity required to make 2 l. be extracted as near boiling as possible.

ANALYSIS OF LEATHER

Woods and such barks as oak and hemlock must be extracted so that the 2 l. will be secured by uniform extraction during 7 hr. instead of 4.

19. Liquid Extracts.—Liquid extracts shall be weighed out as rapidly as possible, avoiding change in moisture content, in a stoppered weighing bottle. Dissolve by washing into a 1-l. flask containing approximately 400 cc. distilled water at 85°C. with enough distilled water at 85°C. to make the volume finally equal to 900 cc. Then proceed as directed under Cooling Solutions (paragraph 21).

Materials sensitive to water at 85°C. may be dissolved at a lower temperature, and this must be stated on the report.

20. Solid, Powdered or Pasty Extracts.—Solid, powdered, and pasty extracts shall be weighed out in a beaker as rapidly as possible, avoiding change in moisture content. Approximately ten times the weight of the extract of distilled water shall be added, the mixture placed on a steam bath and heated with frequent stirring until solution or a uniform suspension is obtained. Wash this solution into a 1-l. flask containing approximately 400 cc. of distilled water at 85°C. with enough distilled water at 85°C. to make the volume finally equal to 900 cc. Then proceed as directed under Cooling of Solutions (paragraph 21).

In the case of extracts containing more than 45 per cent tannin, such quantities shall be taken as to yield 2 l. of infusion of analytical strength.

Cooling of Solutions

21. After dissolving extracts or extracting solid tanning materials, the infusions shall then be cooled to 18°C. as follows:

Immerse the flask in any large vessel or trough containing water at 18°C., and maintain the cooling water at that temperature during the entire period of cooling. Keep the solution in the flask well agitated throughout the cooling process. This procedure is absolutely necessary to ensure uniform results. After cooling, make up the required volume with distilled water, thoroughly mix, and proceed with the filtration.

NOTE.—In hot climates where there are difficulties in maintaining this temperature (18°C.), the flasks may with advantage be enclosed in paper bags after cooling.

B. Analysis

22. General Instructions.—The solutions of total solids, solubles, and non-tannins must be at the same temperature when pipetted.

23. Estimation of Moisture and of Total Solids.—For any tanning extract or material, the sum of the moisture and total solids is 100 per cent, so that a determination of either quantity is sufficient. In the case of solid (crude) tanning materials and also of any solid or pasty extracts that do not yield a uniformly turbid solution, a direct determination of moisture must be made.

24. Moisture.—About 1 g. of the finely ground material is accurately weighed out in a squat-shaped wide-mouthed weighing bottle and dried between 98.5 and 100°C. in a water or steam oven for 3 to 4 hr., cooled in a desiccator for 20 min., and weighed on an analytical balance as quickly as possible. It is then returned to the oven and the drying continued until

constant weight is attained. If any weighing shows an increase in weight over a preceding, the lowest weight found must be taken.

25. Total Solids.—Total solids are determined by evaporating to apparent dryness on a water bath or a combined water bath-steam oven 50 cc. of the well-mixed and uniformly turbid tannin infusion, in the evaporating basins previously described (paragraph 3).

The residues in the basins are then promptly dried between 98.5 to 100°C. for 3 to 4 hr. (see paragraph 4), cooled in desiccators, and weighed as rapidly as possible to an accuracy of 0.2 mg., and this repeated until constant weight is attained. The basins must not be wiped after removal from the desiccator.

It is permissible to use the combined evaporator and dryer and to make one operation of the evaporating and drying.

26. Solubles.—To the amount of the analysis solution required to fill the filter (about 75 cc.) in a beaker add 1 g. of kaolin, mix thoroughly, and pour immediately on to the filter paper (see paragraph 7). Collect the filtrate in the same beaker, and when approximately 25 cc. have been collected, return the filtrate to the paper, repeating this operation for 1 hr., taking care to transfer in this manner all kaolin to the filter. At the end of 1 hr. remove the solution on the filter, disturbing the kaolin as little as possible, as, for example, by siphoning. Bring as much as needed of the original solution to 18°C., as described under Cooling of Solutions (paragraph 21). Refill the filter with this solution, and begin to collect the filtrate for pipetting as soon as the filtrate becomes optically clear,¹ discarding so much filtrate as comes through prior to its coming clear. Keep the filter full, the temperature of the filtering solution at 18°C., and the funnel and collecting vessel covered. Pipette 50 cc. of the clear filtrate into a tared basin, evaporate, dry, cool, and weigh to constant weight, as described above.

27. Preparation of Chromed Hide Powder.—A multiple of that quantity of hide powder containing 6.25 g. of dry matter, according to the number of analyses to be made together with 6 g. for the moisture determination, is digested with ten times its weight of distilled water for 1 hr. To this is added, for each gram of air-dry powder taken, 1 cc. of the stock chrome alum solution (paragraph 11), and the whole well stirred.

Continue to stir frequently for several hours, and then let stand overnight. In the morning transfer the chromed powder to a clean linen or cotton filter cloth, drain, and squeeze. Place the cloth containing the powder in a suitable vessel (an enamel bucket is suitable for large quantities), open out the cloth bag fashion, and pour on to the powder a quantity of water equal to 15 times the weight of the air-dry powder taken. Mix the powder and water thoroughly and digest for 15 min., after which lift out the cloth and powder and immediately drain and squeeze to approximately 75 per cent moisture, using a press if necessary. Digest the powder three more times in the same manner, using distilled water throughout. At the end of the final digestion, squeeze the powder so that it will contain as

¹ The solution is considered to be "optically clear" both by reflected and transmitted light when a bright object such as an electric light filament is distinctly visible through at least 5 cm. thickness, and when a layer 1 cm. deep in a beaker, placed in a good light on black glass or black glazed paper, appears dark and free from opalescence when viewed from above.

nearly as possible 73 per cent moisture, not less than 72 or more than 74 per cent. (It is convenient to squeeze the powder slightly drier than specified, then transfer it as quantitatively as possible to a tared vessel, and carefully add water to give the proper moisture content as determined by weighing.) Thoroughly break up the cake of wet, chromed powder, and mix until uniform and free from lumps. Weigh at once 20 g. of the wet, chromed powder, and determine moisture in it as directed in paragraph 24. Also weigh at once the charges for the non-tannin determinations, transfer them to shake bottles, and stopper the bottles tightly.

28. Non-tannin Determination.—To such quantity of the wet, chromed hide powder as represents as nearly as possible 6.25 g., not less than 6.1 nor more than 6.4 g. of absolutely dry hide powder, add 100 cc. of the analysis solution, and shake immediately for exactly 10 min. in a mechanical rotary shaker at 50 to 65 r. p. m. Pour powder and solution on a clean, dry linen cloth supported by a funnel, drain, and squeeze by hand. Add to the filtrate 1 g. of kaolin that meets the requirements of paragraph 10, mix thoroughly, and pour into a single 15.0-cm. pleated filter paper, returning the filtrate repeatedly until it is clear. Keep the funnel and collecting vessel covered during filtration. (The filtrate must be tested with the gelatin-salt reagent (see paragraph 13), and if 10 cc. gives any turbidity with 1 or 2 drops of the reagent, the fact must be stated on the report of the analysis.) Pipette 50 cc. of the filtrate into a tared dish, evaporate, dry, cool, and weigh. Correct the weight of the residue for the dilution caused by the water in the wet hide powder, and calculate the percentage of non-tannins.

29. Tanning Matter Absorbable by Hide Powder.—Tanning matter absorbable by hide powder is the difference between the percentages of total solubles and non-tannins.

30. Insoluble Matter.—Insoluble matter is the difference between the percentages of total solids and total solubles or between 100 per cent and the sum of the percentages of moisture and soluble matter in the cases of those solid tanning materials and solid and pasty extracts in which moisture is directly estimated.

31. Specific Gravity.—Specific gravity shall be determined by the specific gravity bottle or pycnometer, keeping the temperature as closely as possible to 15°C.

32. Accuracy of the Method.—All analyses shall be the average result of duplicate determinations. The weights of residues shall in all cases agree within 2 mg., so that the absolute error in the tannin content is not more than 2 per cent. For example, for liquid extracts containing 30 per cent of tannin, the duplicate results for percentage of tannin shall agree within 0.6 per cent. For solid extracts of 60 per cent tannin content, the results shall agree within 1.2 per cent. The analysis shall be repeated if necessary until such agreement is reached, and it must be clearly stated on the report that the result is the mean of such determinations. Where analyses are carried out by different chemists on the same sample of extract or tanning material, their results should not differ by more than 3.0 per cent of the total tannin content. When reporting analyses, results shall be stated to one place of decimals only.

33. Conclusion.—All analyses shall be performed in strict accordance with the foregoing instructions, and the report must state that "the analysis has been made by the official international method of tannin analysis." The lot number of the hide powder used in making the analysis must also be stated on the report.

APPENDIX

APPROXIMATE QUANTITIES OF MATERIALS TO BE TAKEN FOR ANALYSIS,
GRAMS PER LITER

Solid tanning materials (woods, barks, fruits, leaves, etc.)

Canaigre.....	15 to 18	Myrabolans (pulp only)...	8 to 10
Chestnut wood (fresh)....	50 to 55	Myrabolans (whole nuts)...	12 to 14
Chestnut wood (dry).....	38 to 42	Valonia (whole cups).....	14 to 15
Quebracho wood and		Valonia beard (trynaeks)...	9 to 10
tizerah.....	19 to 21	Divi-divi, algarobilla, teri,	
Hemlock bark.....	32 to 36	and gonakie.....	10 to 12
Mimosa bark.....	10 to 14	Sumac.....	15 to 16
Oak bark.....	35 to 45	Spent tans.....	50 to 80
Mangrove bark.....	10 to 12		
Pine bark.....	30 to 35		

Solid extracts

Chestnut (60 per cent)....	6 to 7	Sumac.....	6 to 7
Mangrove.....	6	Cutch.....	10
Quebracho (natural).....	6	Gambier (cube).....	12 to 14
Quebracho (soluble).....	6	Gambier (block).....	14 to 16
Mimosa bark.....	6 to 7		

Liquid extracts

Chestnut (30 per cent)....	13	Myrabolans (25 per cent)...	16
Quebracho (natural and		Hemlock.....	11 to 13
soluble).....	12	Pine bark.....	13
Mimosa.....	11 to 13	Sulfite cellulose (wood	
Oak wood.....	16	pulp).....	16 to 18
Sumac.....	16	Synthetic tannins.....	13

COMMENTS ON THE OFFICIAL METHOD

It cannot be too strongly emphasized that the official method for determining tannin is a purely empirical one and that the results obtained by it are subject to great variation if the conditions of the determination are altered ever so slightly. For this reason, it is absolutely essential that the official procedure be followed in minutest detail. Some of the points requiring especial care are discussed below.

Extraction of Raw and Spent Materials. (A. L. C. A. Method).

A common type of extractor that complies with the specifications of the official method of the A. L. C. A. is shown in Fig. 70. The extraction chamber consists of 2 copper parts A and B

tapered to make a tight joint. *A* connects above with a copper coil (not shown), enclosed in an elevated tank of water. The material to be extracted is placed at *D*, between 2 cotton plugs *C* and *C'*. When collecting the percolate outside, the stopcock *F* is turned to the position shown, and the percolate passes through either *E* or *E'* to the volumetric flask *H*. By turning *F* and closing *E* and *E'* by means of pinchcocks or small corks, the percolate may be returned to the boiling flask *G*.

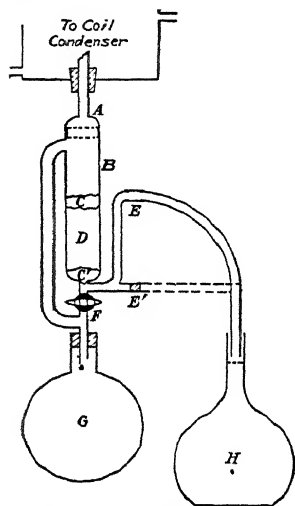


FIG. 70.—Apparatus for extracting raw and spent tanning materials.

Many different forms of extraction apparatus have been devised (31, 63, 65, 68, 86, 101). An all-glass apparatus has been described recently by Frey and Reed (31).

Preparation of Solution.—The specified temperature (85°C.) must not be exceeded, as some kinds of tannin are decomposed at higher temperatures. In cooling, the temperature must not fall below 20°C. (18° according to the international method), and the water bath used for cooling must not be more than 1° colder than this temperature, since many tanning materials are thrown out of solution on chilling and cannot be redissolved unless the solution is heated to 85° or thereabouts.

Evaporation, Drying, and Weighing.—It is necessary that the specified temperature of drying be adhered to, as the weight of residue obtained decreases as the temperature of drying is increased. The residue obtained by evaporating a tannin solution is extremely hygroscopic, and care must be taken that the dish is cooled in an individual desiccator over fresh sulfuric acid for exactly 15 min. and weighed as rapidly as possible. Some tannins seem to oxidize on prolonged heating, with resulting gain in weight (55, 65). The dish should be placed in the desiccator not more than 3 hr. after all liquid has disappeared and should be weighed for the second time after drying for just 1 hr. longer. Should a gain in weight take place, the minimum weight obtained should be taken as correct.

Filtration.—It is obvious that the kaolin must be free from soluble matter, as prescribed in the method. As filter paper and kaolin both absorb tannin from the solution, it is necessary to tan them by a preliminary treatment with the tannin solution. The amount of tannin taken up depends upon the kind of paper and apparently upon the fineness of division of the kaolin (26, 29, 39, 70). Heavier and thicker papers absorb more tannin than do lighter and thinner ones, and the 1-hr. pretannage period with a single portion of solution repeatedly returned to the paper is not sufficient to saturate ordinary brands of filter paper with tannin. Such papers will invariably absorb more tannin when the analytical solution is filtered for the final determination, and the percentage of soluble matter found will be too low. Papers other than the official brands must on no account be used.

The quantity of "insoluble matter" (22, 36, 39, 44, 54, 65, 66, 79, 99) in a tannin solution is a purely arbitrary quantity. Tannin solutions contain particles and molecular aggregates of all sizes from chunks of dirt or other foreign matter that speedily settle out to small molecules. The dispersity of some tanning materials increases with the dilution. These are added reasons why filtration must be carried out exactly as prescribed. Several devices for hastening the filtration have been described recently (43, 54, 65, 66, 79, 99).

Instead of filtering through paper and kaolin, European analysts have been accustomed to filter through a porous filter candle of the Berkefeld type (38, 90). The candle must be pretanned, just as the paper is, and must be cleaned with chromic acid or other agent after using. The candle gives slightly different values for insoluble matter than does paper, but in view of the arbitrary nature of what is called insoluble matter, this is not important, provided all analysts agree to use one or the other exclusively. Tests in the authors' laboratory indicate that the concordance obtainable with the candle is at least as good as that obtainable with paper. The choice seems to come down to the question of which method is most convenient and economical of time and money. At present, the candle method is not permissible in determining tannin by the official method.

Detannizing the Solution.—When 100 cc. of solution containing 0.4 g. of tannin are shaken for 10 min. with 6.25 g. of dry hide powder (chromed, washed, and squeezed to a water content of 73 per cent), as prescribed in the official method) all the tannin in

the solution is absorbed by the hide powder. This is shown by the fact that the filtrate from that hide powder does not give a precipitate with the gelatin-salt reagent. But, in addition to tannin, *i.e.*, substances that will precipitate gelatin, the hide powder also removes large quantities of substances that will not precipitate gelatin and that are combined so loosely with hide substance that they can easily be removed therefrom by washing (105). If all the conditions of the official method are fulfilled exactly, the quantity of such material absorbed by the powder is quite constant for a given sample of a given tanning material, thus permitting different analysts to obtain the same value for tannin, which, as stated before, is the indispensable requirement in any method for evaluating tanning materials. But if any of the conditions are not observed, the quantity of non-tannin absorbed will be changed. The higher the concentration of the solution, for a given quantity of hide powder, the lower the proportion of the total non-tannin that is absorbed by the powder. The higher the ratio of powder to liquor the greater is the proportion of such material that is absorbed. The longer the period of contact (within limits) the greater the quantity of material absorbed by the hide powder. Therefore, the tannin solution must contain 0.4 per cent tannin (within the limits specified), the ratio of solution to dry hide powder must be exactly 100: 6.25, the hide powder must contain exactly 73 per cent water, and the time of contact must be exactly 10 min. Wilson and Kern (105) have shown that by altering these conditions, it is possible to obtain almost any percentage of tannin desired.

The quantity of material absorbed depends also upon the nature and method of preparation of the hide powder (7, 13, 36, 57, 67, 70, 95, 96). This is due in part to different specimens of hide powder containing more or less mineral matter, especially acids and bases, but apparently also to differences in specific surface and to differences in degree of degradation of the collagen. This is overcome, or minimized, in practice by preparing hide powder in very large batches, each of which is tested and released for use only if it is found to give results agreeing with those obtained with the previous officially accepted batch.

The quantity of material absorbed by the hide powder varies with the pH value of the tannin solution (5, 36, 41, 80, 97, 102, 106), increasing with pH value to pH = 7 and thereafter declining. This point is not covered in the official method. In

analyzing duplicate samples of one shipment of a given extract, this does not lead to discordance unless the pH values of the samples have become different, as the result, generally, of fermentation. Differences in pH value between different shipments of the same material do, however, result in fictitious differences in their apparent tannin contents.

Calculations.—The quantity of wet, squeezed hide powder to take for detannizing 200 cc. of solution is the weight equivalent to (12.5 g. \pm 0.3) g. of dry hide powder and is calculated from the equation

$$W = \frac{12,500}{x}$$

where x is percentage of water in squeezed powder. The weights to use for different water contents in the permissible range are given below:

Per cent water in squeezed hide powder	Grams squeezed hide powder containing 12.5 g. dry hide powder	Permissible variation (0.3 g. dry hide powder)
71	43.1	± 1.0
72	44.6	± 1.1
73	46.3	± 1.1
74	48.1	± 1.2

In calculating percentage of non-tannin, the water introduced with the hide powder must be taken into the consideration. This is done by multiplying the weight of non-tannin found by a factor, which is (200 + grams of water in hide powder) \div 200. The calculation of percentage of non-tannin then becomes

$$\text{Per cent non-tannin} = \frac{\text{g. H}_2\text{O in h.p.}}{2} \times 100$$

g. sample in aliquot evaporated

Values for the factor, (200 + grams of water in hide powder) \div 200, are given below for the permissible moisture range.

Per cent water in squeezed hide powder	Non-tannin factor: 200 + g. H ₂ O in hide powder
	200
71	1.15
72	1.16
73	1.17
74	1.18

Percentages of total solids and soluble matter are found directly by multiplying residue weights by 100 and dividing by the weight of extract or raw material in the volume of solution that was evaporated. The difference between percentage of total solids and percentage of soluble matter is taken as percentage of insoluble matter, and the difference between percentage of soluble matter and percentage of non-tannin is taken as percentage of tannin. Percentage of water is taken as the difference between percentage of total solids and 100.

THE WILSON-KERN METHOD (56, 83, 84, 85, 90, 102, 105)

The Wilson-Kern method is based upon the definition of tannin as that material which will precipitate gelatin and which forms a compound with hide substance that is resistant to washing. In the official method, as stated before, a large part of the material absorbed by the hide powder is incapable of precipitating gelatin and is easily removed from the hide powder by washing. In the Wilson-Kern method, tannin is determined by shaking a weighed quantity of hide powder, previously freed from fat and soluble matter by a purification process, with a quantity of analytical tannin solution such that all the tannin (*i.e.*, material capable of precipitating gelatin) is removed in a few hours. The tanned hide powder is then washed until free from all readily soluble matter and dried. As first proposed (105), the method then provided for the analysis of the air-dry powder (which did not have to be collected quantitatively) for hide substance, fat, water, and ash, by the same methods that are employed for vegetable-tanned leathers (Chap. II). Percentage of tannin in the tanned powder was determined by difference, the ratio of tannin to hide substance ascertained, and the weight of tannin combined with the whole sample of hide powder taken was calculated. As this method is somewhat laborious and time consuming, the so-called "modified Wilson-Kern method" was devised (102, 105), in which all of the tanned hide powder is collected after washing,

dried in an oven, and weighed. The increase in weight of the hide powder is taken as tannin. The percentage accuracy of the modified method is somewhat less than that of the original method, because smaller quantities of tan liquor and hide powder must be taken. The modified method is also more subject to error through mechanical losses, though these can be detected simply by determining collagen in the entire tanned powder after it is weighed. The greater speed and simplicity of the modified method far outweigh these drawbacks.

The Wilson-Kern method depends for its validity upon the exact nature of the facts corresponding to the phrase "resistant to washing" in the definition of tannin. In this method, the

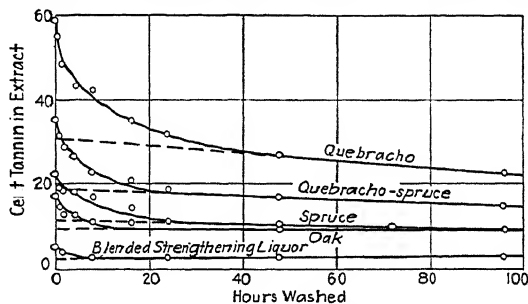


FIG. 71.—Effect of time of washing on percentage of tannin found in vegetable tanning extracts by the Wilson-Kern method.

tanned powder is washed until all soluble non-tannin is removed. This point is shown by failure of the washings to respond to the ferric chloride test for non-tannin. If the hydrolyzability of the hide-tannin compound is so great that appreciable amounts of tannin are removed during this washing, it is obvious that the quantity of tannin finally weighed will be too low; furthermore, if the common tanning materials contain substances that combine with hide powder to form compounds with all possible degrees of resistance to hydrolysis, so that the curve obtained by plotting weight of tanned hide powder against time of washing is devoid of any breaks, it would follow that no sharp line of demarkation between tannin and non-tannin could be drawn at all. The original experiments of Wilson and Kern (105) indicated that the tanned powder ceased to give up anything to the wash water after it had been washed with 25 changes of water. Recent work in this laboratory (56), in which the tanned

powder was washed continuously for varying periods up to 4 days, has shown that the tanned powder does continue to decrease in weight, up to the longest washing period employed. The rate of loss after the first day is, however, small and practically constant, so that the washing-out curves show a well-defined break corresponding to complete removal of non-tans. The quantity of tannin lost during the removal of non-tannin, while appreciable, is not so great as to destroy the usefulness of the results obtainable by the method. The behavior of the tanned powder on prolonged washing is shown in Fig. 71.

Preparation of Solution.—Weigh accurately from 7 to 20 g. of extract, and dissolve in 1 l., exactly as directed in the official method of tannin analysis. The quantity of extract taken should be such as will give a solution of such strength that a 100-cc. portion will just be detannized completely by 2 g. of dry hide powder upon shaking for from 6 to 16 hr. In analyzing a new material, solutions of several different strengths should be prepared and tested, and the results obtained with the strongest solution that can be detannized completely under the specified conditions should be used. The following quantities of extracts have been found by the authors to be the proper amounts to use:

	Grams
Liquid hemlock.....	20
Liquid larch.....	20
Solid larch.....	12
Liquid oak bark.....	20
Sumac (leaves).....	20
Sumac (extract).....	22
Liquid superspruce.....	17.5
Gambier (paste).....	16
Gambier (cube).....	12
Solid quebracho.....	7
Solid wattle.....	10

Preparation of Hide Powder (102).—Treat a large quantity of standard hide powder successively with water, 50-per cent alcohol, 95-per cent alcohol, alcohol-xylene, and xylene, as described under determination of enzyme activity toward collagen in Chap. VI. Let the final xylene evaporate in the air, break up any lumps that may have formed, and shake the powder vigorously on a 100-mesh screen, rejecting the siftings. Store the portion retained by the screen in a well-stoppered bottle.

Gelatin-salt Reagent (92).—Soak 1 g. of good-grade photographic gelatin in 100 cc. of water at 40°C. until dissolved, then add 10 g. of pure sodium chloride, and stir until it is dissolved. Prepare the solution afresh daily.

Insoluble Matter, Total Solids, and Soluble Matter.—Determine exactly as directed in the official method.

Tannin.—Filter about 110 cc. of the tannin solution exactly as directed under determination of soluble matter in the official method, using Munk-

tell's No. 1F paper and approved kaolin, and pretanning the paper for 1 hr., rejecting the portion of the solution used for pretanning. Weigh accurately about 2.5 g. of purified hide powder into a wide-mouth bottle of 250 to 350 cc. capacity. At the same time, weigh accurately about 3 g. of hide powder, and dry to constant weight at 105°C., calculate percentage of water in the hide powder, and calculate the exact weight of dry hide substance in the sample weighed for the analysis.

Measure exactly 100 cc. of the filtered tannin solution into the bottle containing the hide powder, stopper tightly, and place the bottle in a shake box rotating approximately 60 times per minute. Rotate the hide powder and liquor for not less than 6 hr.; this permits the washing to be started late in the afternoon of the day on which the analysis is commenced; an equally satisfactory procedure is to rotate the powder and liquor overnight. Pour the liquor and hide powder into a Wilson-Kern extractor (Fig. 7), using a piece of 10-oz. S. F. white cotton duck filter cloth¹ stretched tightly across the lower end of *B* (Fig. 7) to effect filtration. It is essential that the filter cloth be fine-meshed enough to retain all particles of the tanned hide powder. Muslin must on no account be used. Support the Wilson-Kern extractor in the mouth of a small filter flask, and filter the liquor under gentle suction. Return the filtrate to the cloth until it comes through optically clear. To about 10 cc. of the clear filtrate add 1 drop of gelatin-salt reagent. If a precipitate or turbidity is produced, the solution is not completely detanned, and the determination must be rejected. If no precipitate is formed, transfer quantitatively to the extractor the tanned hide powder remaining in the shake bottle, using a wash bottle and policeman. Take care that any hide powder adhering to the stopper is transferred. Connect the extractor to a reservoir of distilled water, close the lower stopcock, fill the extractor about half full of water, open the lower stopcock, and regulate the upper stopcock so that water drips from the outlet tube at a rate of about 10 cc. per minute. See that the joint between *A* and *B* (Fig. 7) is tight, and clamp the extractor so that a slight downward pressure is exerted on this joint. These precautions are necessary because the mat of hide powder on the fine filter cloth causes considerable back pressure, which may cause the joint *AB* to separate, with consequent flooding of the apparatus. Wash the tanned powder with water flowing at a rate of about 10 cc. per minute for at least 12 hr. Then close both stopcocks and let the tanned powder stand in contact with the water in the extractor for 1 hr. Disconnect *B* and *C* from *A*, open the stopcock in *C*, and draw off about 10 cc. of the solution into a test tube, discarding any water that may be standing in *C*. To this solution add 1 drop of a 1-per cent solution of ferric chloride, mix, and examine by holding the tube against a white background. If the solution shows any sign of blue or green, the washing is not complete. In such a case, continue the washing for several hours more, and test again. In making the test, disregard a slight yellow-brown color that is sometimes produced.

When the washing is complete, transfer the powder quantitatively to a hardened filter paper in a Buechner funnel. The paper should be cut to fit the bottom of the funnel snugly and should be moistened and pressed down so as to make good contact with every part of the supporting surface.

¹ John Boyle and Company, New York.

Use a wash bottle and policeman to effect the transfer. Filter with the aid of suction, and continue to apply suction until the powder forms a coherent mat that separates readily from the paper. Do not let the powder become too dry, as it then becomes difficult to separate it from the paper. The exact length of time to apply the suction is easily learned from experience.

Separate the mat of tanned powder from the paper by means of a rather sharp-bladed spatula, and transfer it to a weighed dish. Loosen with a spatula any particles of hide powder that remain adhering to the paper, and brush them into the dish. Similarly, collect any particles that may be adhering to the sides of the funnel. Place the dish in an oven at a temperature not exceeding 50°C. until the powder is air dry, then place it in an oven at 105°C. for 12 to 16 hr. Cool in an individual desiccator over strong sulfuric acid for exactly 15 min., and weigh rapidly. Reheat for 1 hr., and reweigh. Repeat till constant weight is attained. Calculate and report percentage of tannin from the gain in weight of the hide powder.

G. tannin = g. tanned powder - [g. air-dry powder \times (100 - per cent H₂O in powder) \times 0.01]

$$\text{Per cent tannin} = \frac{\text{g. tannin} \times 100}{\text{g. extract in 100 cc. of solution}}$$

Per cent non-tannin = per cent soluble matter - per cent tannin

Detection of Mechanical Losses.—Transfer the entire sample of tanned hide powder, after weighing, to a Kjeldahl flask, and digest by boiling with 10 g. of sodium sulfate or potassium sulfate, 30 cc. of pure, concentrated sulfuric acid, and a small crystal of copper sulfate, until the solution is clear and practically colorless. Cool, dilute with about 200 cc. of water, cool again, and transfer the solution quantitatively to a 250-cc. volumetric flask, and make up to the mark. Pipette exactly 50 cc. of this solution into a Kjeldahl flask, dilute to 250 cc., arrange the flask for distillation as described under determination of hide substance in Chap. II, make the solution alkaline with strong sodium hydroxide, and distill the liberated ammonia into 100 cc. of tenth-normal sulfuric acid. Back-titrate the excess of acid with tenth-normal sodium hydroxide, deduct the blank, and calculate the weight of hide substance in the tanned hide powder. The weight found should agree with the weight of dry hide powder taken within 0.0050 g.

G. hide substance = cc. 0.1-N H₂SO₄ consumed \times 5 \times 0.787

Determination of Tannin in Liquors.—Filter the liquor (undiluted) as described under determination of soluble matter by the official method, pretanning the paper as usual. Measure into the bottle containing the weighed charge of hide powder as great a volume of filtered liquor as will be detanned completely in 6 to 16 hr. The exact quantities must be determined for the particular liquors of any given tannery by preliminary tests. In the authors' laboratory, the quantities of liquor taken vary from 100 cc. for the weakest to 40 cc. for the strongest liquors. In the case of strengthening liquors, prepare a solution of such strength that 100 cc. will be just detanned by 2 g. of hide powder, as in the case of extracts, and use 100 cc. of this solution. Proceed with the analysis exactly as described above, and calculate percentage of tannin in the liquor.

$$\text{Per cent tannin} = \frac{\text{g. tannin}^1 \times 100}{\text{cc. liquor taken}}$$

Comments.—Very old and much-exhausted liquors often give a negative value for tannin according to the Wilson-Kern method. The reason for this is that these liquors contain too little tannin to protect the hide powder against hydrolysis during washing.

The sensitivity of the gelatin-salt test varies with the kind of tanning material and with the pH value of the solution to which it is applied (92). The maximum sensitivity occurs in the pH range from 3.5 to 4.5. In doubtful cases, particularly when determining how much of an extract it is permissible to use for the determination, it is necessary to bring the filtrate from the tanned hide powder to a pH value in this range before applying the test. This can be done either by means of indicators or by the hydrogen electrode (see Chap. VII). In the pH range 3.5 to 4.5, the sensitivity of the test varies from 1 part in 110,000 for gambier to 1 in 200,000 for wattle.

The sensitivity of the ferric chloride test for soluble non-tannin is about 1 part in 75,000 for pure pyrogallol and about 1 part in 20,000 for the non-tans of ordinary tan liquors.

OTHER METHODS FOR TANNIN DETERMINATION

The older methods for tannin determination (75, 90), which depend upon reactions of tannin other than that between tannin and hide substance, such as the Loewenthal method (90), are practically obsolete.

Determination of tannin by ultrafiltration has been advocated by Brown (17) and contested by Thomas and Kelly (94).

Modified apparatus for the determination of tannin by the official method has been proposed by Baldracco (8, 9, 10, 82) and by Stiasny (9, 62, 89, 90).

IDENTIFICATION OF TANNING MATERIALS

A great many qualitative tests have been described for the identification of specific tanning materials and the detection of adulteration of the more expensive extracts with cheaper materials. To include a tabulation of these tests would have increased the size of this volume unduly. For a discussion of them the reader is referred to the authors cited at the conclusion of this chapter (19, 20, 32, 33, 46, 72, 75, 90, 91, 102).

¹ Calculated as in the case of extracts.

SPECIFIC GRAVITY

The determination of specific gravity of liquid extracts and tan liquors affords a rapid means of determining the total solids content. To be of value, the results of the determination must be compared with results previously determined with liquors or extracts of known solids content. The specific gravity is, of course, affected by the presence of soluble organic non-tannin, as well as soluble organic or inorganic acids and salts, and hence is not a method for estimating tannin, except perhaps in freshly prepared liquors made from materials in which the ratio of tannin to non-tannin is known.

Liquid Extracts.—Determine specific gravity at 15°C. by means of the pycnometer, as directed in the international method for tannin analysis, or by means of a specific-gravity balance of the Westphal or Young "gravitometer" type.

Gravitometer Method.—Place about 200 cc. of extract in the cylinder supplied with the apparatus, immerse in cold water, and stir slowly with a thermometer until the temperature of the extract is exactly 15°C. Take care that no air bubbles are stirred into the extract. Suspend the plummet in the extract from the balance arm, taking care that it is immersed completely, and obtain the specific gravity from the weights required to bring the instrument into balance. Report specific gravity at 15°C. to three decimal places.

Solid and Liquid Extracts: Specific Gravity of a Solution of Definite Strength.—Weigh accurately a definite quantity of extract and dissolve in water at 85°C., as described under the preparation of the analytical solution for the determination of tannin. Transfer the solution to a 500-cc. volumetric flask, let it cool slowly to room temperature, bring it to 20°C., and make up to the mark. The quantity of extract employed in the authors' laboratory is 60 g., equivalent to 1 lb. per gallon. Determine specific gravity of a portion of this solution at 15°C., as described in the preceding paragraph, or, if preferred, determine its "barkometer," as described below.

Tan Liquors: Barkometer.—Determine the specific gravity of tan liquors by means of a special hydrometer equipped with the so-called "barkometer" scale. This scale gives directly the second and third decimal places of the specific gravity; *i.e.*, a barkometer reading of 24.5 means specific gravity = 1.0245. Barkometers are designed for use at 60°F. Instead of bringing the liquor to this temperature, it is sufficiently accurate to determine the barkometer reading of the liquor at whatever temperature it may be, determine its temperature, and correct the observed barkometer for temperature by means of the data given in Table 43.

For the temperature range 50 to 75°F. (the usual range met with in tan liquors) add $\frac{1}{2}^{\circ}$ to the observed reading for each 5° by which the temperature exceeds 60°F., or subtract $\frac{1}{2}^{\circ}$ for each 5° by which the temperature falls below 60°F.

TABLE 43.—TEMPERATURE CORRECTIONS FOR BARKOMETER READINGS OF TAN LIQUORS
(After Yocum)

Observed reading	At temperature indicated, add the following values to the observed reading to obtain the barkometer reading at 60°F.:																
	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115	120
0	0	½	1	1½	2	3	3½	4¼	5	6	7	8¼	9
5	-2	-1½	-1	-¾	0	½	1	1½	2	3	3½	4¼	5	6	7	8¼	9
10	-2	-1½	-1	-¾	0	½	1	1½	2	3	3½	4¼	5¼	6¾	7¾	8½	9¾
15	-2½	-1¾	-1	-¾	0	½	1	1½	2¼	3	3¾	4½	5¼	6¾	7¾	8½	9¾
20	-2½	-1¾	-1	-¾	0	½	1	1½	2¼	3	3¾	4½	5½	6¾	7¾	8½	9¾
25	-2½	-1¾	-1	-¾	0	½	1	1½	2¼	3¼	3¾	4½	5½	6¾	7¾	8½	9¾
30	-2½	-1¾	-1	-¾	0	½	1	1½	2¼	3¼	4	5	6	6¾	8	9	10
35	-2½	-1¾	-1	-¾	0	½	1	1½	2¼	3¼	4	5	6	6¾	8	9	10
40	-2½	-1¾	-1	-¾	0	½	1	1½	2¼	3¼	4	5	6	6¾	8	9¼	10
45	-2½	-1¾	-1	-¾	0	½	1	1½	2¼	3¼	4	5	6	6¾	8¼	9¼	10
50	-2½	-1¾	-1	-¾	0	½	1	1½	2¼	3¼	4	5	6	6¾	8¼	9¼	10¾
55	-2½	-1¾	-1	-¾	0	½	1	1½	2¼	3¼	4	5	6	6¾	8¼	9¼	10¾
60	-2½	-1¾	-1	-¾	0	½	1	1½	2¼	3¼	4	5	6	6¾	8¼	9¼	10¾

Many commercial barkometers are more or less inaccurately scaled, hence all barkometers should be calibrated by determining the readings that they give with a series of solutions whose specific gravities have been determined accurately with the pycnometer or Westphal balance.

ASH

Total Ash of Extracts.—Weigh accurately about 3 g., or measure exactly 25 cc. of the solution prepared for the determination of specific gravity, into a weighed porcelain or platinum evaporating dish. Evaporate to dryness in an oven or on the water bath, then heat at dull red heat, preferably in a muffle furnace, until all carbon is consumed. Cool in a desiccator, and weigh. Calculate and report percentage of total ash.

$$\text{Per cent total ash} = \frac{\text{g. ash} \times 100}{\text{g. sample}}$$

Soluble Ash of Extracts.—Filter a portion of the solution prepared for the determination of specific gravity through thin filter paper, rejecting the first 25 cc. of filtrate. Pipette 25 cc. of filtrate into a weighed platinum dish, and determine ash as described above. Calculate and report percentage of soluble ash.

$$\text{Per cent soluble ash} = \frac{\text{g. ash} \times 100}{\text{g. extract in 25 cc.}}$$

Total Ash of Liquors.—Pipette from 10 to 50 cc. of liquor into a weighed dish, and determine ash as described in the second paragraph above.

$$\text{Per cent ash} = \frac{\text{g. ash} \times 100}{\text{cc. liquor taken for determination}}$$

Analysis of Ash.—Unless the amount of insoluble ash (difference between total and soluble ash) is unusually large, it is sufficient to analyze the soluble ash of extracts. The determinations called for are those of iron and aluminum, calcium, magnesium, and sodium carbonate. The purpose of analyzing extract ash is to prevent contamination of the liquors with undue amounts of mineral salts. The purpose of the analysis of the ash of tan liquors is rather to follow the accumulation of mineral matter carried into the liquor by the skins. The principal substances so introduced ordinarily are lime and chlorides, though the nature of such substances will depend, of course, upon the treatment given the skins before tanning.

Soluble Ash of Extracts: Sodium Carbonate.—Treat the ash with exactly 10 cc. of tenth-normal sulfuric acid, heat gently for about 5 min., add a few drops of methyl red indicator, and add more acid in case the solution is not acid. Rinse the solution into a beaker, dilute to about 100 cc., and boil for about 2 min. to expel carbon dioxide. Cool, and titrate the excess acid with tenth-normal sodium hydroxide till the indicator turns yellow. Calculate and report percentage of sodium carbonate, correcting for the alkalinity due to calcium and magnesium present.

Per cent $\text{Na}_2\text{CO}_3 =$

g. extract taken for ash determination

Iron and Aluminum, Calcium, and Magnesium.—If any insoluble matter remains in the dish used for the ash determination, after the treatment with tenth-normal sulfuric acid described above, filter the solution, ash the filter paper, fuse the residue with a little sodium carbonate, dissolve the fusion in dilute hydrochloric acid, and add the solution to that in which sodium carbonate was determined. Determine iron and aluminum (together), calcium, and magnesium, as directed under analysis of the ash of vegetable-tanned leathers (Chap. II). Calculate and report percentages of iron and aluminum as oxides, calcium as oxide, and magnesium as oxide.

Liquor Ashes: Alkalinity as Calcium Oxide.—Proceed exactly as directed under determination of sodium carbonate in ash of extracts, but calculate and report the total alkalinity as calcium oxide.

Per cent alkalinity as $\text{CaO} = \frac{(\text{cc. } 0.1\text{-}N \text{ H}_2\text{SO}_4 - \text{cc. } 0.1\text{-}N \text{ NaOH}) \times 0.28}{\text{cc. liquor taken for ash}}$

Chlorides.—After determining alkalinity as above, add to the solution a few drops of a 10-per cent solution of potassium chromate, and titrate with tenth-normal silver nitrate to the formation of a brick-red precipitate. Calculate and report percentage of chlorides as sodium chloride.

Per cent $\text{NaCl} = \frac{\text{cc. } 0.1\text{-}N \text{ AgNO}_3 \times 0.5846}{\text{cc. liquor taken for ash}}$

VEGETABLE TANNING MATERIALS

Weigh accurately about 3 g. of extract into a platinum dish and stir thoroughly with about 40 g. of pure anhydrous sodium carbonate, using a stiff platinum wire. Brush off any of the mixture adhering to the wire. Cover the mixture with a thin layer of pure sodium carbonate. Heat to dull redness in a muffle furnace until all organic matter is carbonized. Cool. Dissolve the contents of the dish in hot water, and filter the solution into a 500-cc. volumetric flask, cool, and make up to the mark. Pipette 200 cc. into a 400-cc. beaker, add several cubic centimeters of saturated bromine water, acidify with hydrochloric acid, and boil until the yellow color disappears. To the hot solution add drop by drop, from a pipette, about 10 cc. of 10-per cent barium chloride solution. Allow the precipitate to settle for several hours. Filter through Whatman's No. 44 paper or its equivalent, and wash free from chlorides. Place the paper and precipitate in a weighed crucible, dry at 105°C., and ignite, beginning at a low temperature and ending at bright red heat. Allow free access of air to the contents of the crucible during ignition. Cool in a desiccator and weigh. Calculate and report percentage of sulfate as SO_4 .

$$\text{Per cent } \text{SO}_4 = \frac{\text{g. BaSO}_4 \times 0.343 \times 0.4}{\text{g. sample weighed}}$$

CHLORINE

Pipette 200 cc. of the solution prepared as described under determination of sulfate into a 400-cc. beaker, and acidify with acetic acid. Heat gently, and add more acid if necessary to keep the solution slightly acid. Add a few drops of a 10-per cent solution of potassium chromate, and titrate with tenth-normal silver nitrate to the formation of a permanent brick-red precipitate. Calculate and report percentage of chlorine.

$$\text{Per cent Cl} = \frac{\text{cc. 0.1-N AgNO}_3 \times 0.3546 \times 0.4}{\text{g. sample weighed}}$$

GLUCOSE IN EXTRACTS (24, 51)

Measure roughly 150 cc. of the analytical solution prepared as described in the official method for tannin analysis, and treat with about 2 g. of solid lead acetate. Stir. Filter through a dry pleated filter into a dry beaker. To the filtrate add enough solid potassium oxalate to precipitate all the lead and filter as before. Test the filtrate for complete deleading by adding a small crystal of potassium oxalate; if a precipitate forms, add more oxalate and filter again. Pipette 100 cc. of the filtrate into a 500-cc. Erlenmeyer flask, add 5 cc. of concentrated hydrochloric acid, place a small short-stemmed funnel in the mouth of the flask to act as a reflux condenser, and boil gently for 1 hr. Cool the solution, add a drop of phenolphthalein, and add solid anhydrous sodium carbonate cautiously until the solution is alkaline. Filter the solution into a 250-cc. volumetric flask, wash the paper free from alkali, and make up to the mark. Pipette 100 cc. of the solution into a 250-cc. beaker, and treat with 15 cc. of Fehling's copper sulfate solution and 15 cc. of Fehling's alkaline tartrate solution (Chap. II). Heat

over a flame so regulated that the solution begins to boil exactly 4 min. after the flame is lighted, and boil for exactly 2 min. Filter the precipitated copper at once through Whatman No. 44 paper or its equivalent, and wash free from alkali with hot water. Ignite in a tared porcelain crucible, cool in a desiccator, and weigh as cupric oxide, CuO . Convert the weight to cuprous oxide, Cu_2O , by multiplying by 0.9. Obtain the weight of glucose corresponding to this weight of cuprous oxide from Munson and Walker's table given below. Calculate and report percentage of glucose in the extract.

$$\text{Per cent glucose} = \frac{\text{g. glucose} \times 100}{\text{g. extract in 40 cc. of the original solution}}$$

pH VALUE OF EXTRACTS AND TAN LIQUORS

Determine pH value of liquors directly by the electrometric method, described in Chap. VII. Determine the pH value of the analytical solution of extracts, prepared as described above under the official method for tannin analysis, and report "pH value of a solution containing——g. of extract."

TOTAL ACID IN TAN LIQUORS¹

Pipette exactly 50 cc. of liquor into the vessel used for determining pH value, and titrate with normal sodium hydroxide to a pH value of 7.0, as described in Chap. VII. Calculate and report percentage of total acid as lactic acid.

$$\text{Per cent total acid as lactic} = \text{cc. 1-N NaOH} \times 0.18$$

NOTE.—As the pH value and acid content of solutions containing tannin change rapidly due to fermentation, it is essential that pH value and total acid content be determined as soon as the sample is received.

COLOR OF TANNING EXTRACTS

The color of tanning extracts is less important than might be supposed, first because the color of the leather is only very roughly related to that of the extract, and second because the color is affected much more by the pH value of the liquors used in tanning than it is by the color of the extract. Other factors being equal, the color of the leather is affected by the color of the extract (104). Some extracts (*e.g.*, chestnut) when carelessly made have a very dark color the results of which cannot be avoided by tanning at any safe pH value.

Two types of methods that have been employed for measuring the color of extracts call for a description. The first is the Lovibond tintometer method (64, 75, 90), extensively used in Great Britain. A filtered solution of the extract (usually the

¹ For the determination of total acidity by means of indicators, see under the official methods of tannin analysis, and the literature cited at the conclusion of this chapter (6, 11, 12, 21, 40, 45, 50).

MUNSON AND WALKER'S TABLE¹

Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (<i>d</i> -glucose) Mg.	Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (<i>d</i> -glucose) Mg.
10	8.9	4.0	45	40.0	19.1
11	9.8	4.5	46	40.9	19.6
12	10.7	4.9	47	41.7	20.0
13	11.5	5.3	48	42.6	20.4
14	12.4	5.7	49	43.5	20.9
15	13.3	6.2	50	44.4	21.3
16	14.2	6.6	51	45.3	21.7
17	15.1	7.0	52	46.2	22.2
18	16.0	7.5	53	47.1	22.6
19	16.9	7.9	54	48.0	23.0
20	17.8	8.3	55	48.9	23.5
21	18.7	8.7	56	49.7	23.9
22	19.5	9.2	57	50.6	24.3
23	20.4	9.6	58	51.5	24.8
24	21.3	10.0	59	52.4	25.2
25	22.2	10.5	60	53.3	25.6
26	23.1	10.9	61	54.2	26.1
27	24.0	11.3	62	55.1	26.5
28	24.9	11.8	63	56.0	27.0
29	25.8	12.2	64	56.8	27.4
30	26.6	12.6	65	57.7	27.8
31	27.5	13.1	66	58.6	28.3
32	28.4	13.5	67	59.5	28.7
33	29.3	13.9	68	60.4	29.2
34	30.2	14.3	69	61.3	29.6
35	31.1	14.8	70	62.2	30.0
36	32.0	15.2	71	63.1	30.5
37	32.9	15.6	72	64.0	30.9
38	33.8	16.1	73	64.8	31.4
39	34.6	16.5	74	65.7	31.8
40	35.5	16.9	75	66.6	32.2
41	36.4	17.4	76	67.5	32.7
42	37.3	17.8	77	68.4	33.1
43	38.2	18.2	78	69.3	33.6
44	39.1	18.7	79	70.2	34.0

¹ From Association of Official Agricultural Chemists, "Methods of Analysis," 2d ed p. 434, 1925.

N AND WALKER'S TABLE.¹—(Continued)

Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.	Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.
80	71.1	34.4	115	102.2	50.0
81	71.9	34.9	116	103.0	50.5
82	72.8	35.3	117	103.9	50.9
83	73.7	35.8	118	104.8	51.4
84	74.6	36.2	119	105.7	51.8
85	75.5	36.7	120	106.6	52.3
86	76.4	37.1	121	107.5	52.7
87	77.3	37.5	122	108.4	53.2
88	78.2	38.0	123	109.3	53.6
89	79.1	38.4	124	110.1	54.1
90	79.9	38.9	125	110.0	54.5
91	80.8	39.3	126	111.9	55.0
92	81.7	39.8	127	112.8	55.4
93	82.6	40.2	128	113.7	55.9
94	83.5	40.6	129	114.6	56.3
95	84.4	41.1	130	115.5	56.8
96	85.3	41.5	131	116.4	57.2
97	86.2	42.0	132	117.3	57.7
98	87.1	42.4	133	118.1	58.1
99	87.9	42.9	134	119.0	58.6
100	88.8	43.3	135	119.9	59.0
101	89.7	43.8	136	120.8	59.5
102	90.6	44.2	137	121.7	60.0
103	91.5	44.7	138	122.6	60.4
104	92.4	45.1	139	123.5	60.9
105	93.3	45.5	140	124.4	61.3
106	94.2	46.0	141	125.2	61.8
107	95.0	46.4	142	126.1	62.2
108	95.9	46.9	143	127.0	62.7
109	96.8	47.3	144	127.9	63.1
110	97.7	47.8	145	128.8	63.6
111	98.6	48.2	146	129.7	64.0
112	99.5	48.7	147	130.6	64.5
113	100.4	49.1	148	131.5	65.0
114	101.3	49.6	149	132.4	65.4

¹ From Association of Official Agricultural Chemists, "Methods of Analysis," 2d ed. p. 434, 1925.

MUNSON AND WALKER'S TABLE.¹—(Continued)

Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.	Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.
150	133.2	65.9	185	164.3	82.0
151	134.1	66.3	186	165.2	82.5
152	135.0	66.8	187	166.1	82.9
153	135.9	67.2	188	167.0	83.4
154	136.8	67.7	189	167.9	83.9
155	137.7	68.2	190	168.8	84.3
156	138.6	68.6	191	169.7	84.8
157	139.5	69.1	192	170.5	85.3
158	140.3	69.5	193	171.4	85.7
159	141.2	70.0	194	172.3	86.2
160	142.1	70.4	195	173.2	86.7
161	143.0	70.9	196	174.1	87.1
162	143.9	71.4	197	175.0	87.6
163	144.8	71.8	198	175.9	88.1
164	145.7	72.3	199	176.8	88.5
165	146.6	72.8	200	177.7	89.0
166	147.5	73.2	201	178.5	89.5
167	148.3	73.7	202	179.4	89.9
168	149.2	74.1	203	180.3	90.4
169	150.1	74.6	204	181.2	90.9
170	151.0	75.1	205	182.1	91.4
171	151.9	75.5	206	183.0	91.8
172	152.8	76.0	207	183.9	92.3
173	153.7	76.4	208	184.8	92.8
174	154.6	76.9	209	185.6	93.2
175	155.5	77.4	210	186.5	93.7
176	156.3	77.8	211	187.4	94.2
177	157.2	78.3	212	188.3	94.6
178	158.1	78.8	213	189.2	95.1
179	159.0	79.2	214	190.1	95.6
180	159.9	79.7	215	191.0	96.1
181	160.8	80.1	216	191.9	96.5
182	161.7	80.6	217	192.8	97.0
183	162.6	81.1	218	193.6	97.5
184	163.4	81.5	219	194.5	98.0

¹ From Association of Official Agricultural Chemists, "Methods of Analysis," 2d ed. p. 434, 1925.

AND WALKER'S TABLE.¹—(Continued)

Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.	Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.
220	195.4	98.4	255	226.5	115.2
221	196.3	98.9	256	227.4	115.7
222	197.2	99.4	257	228.3	116.1
223	198.1	99.9	258	229.2	116.6
224	199.0	100.3	259	230.1	117.1
225	199.9	100.8	260	231.0	117.6
226	200.7	101.3	261	231.8	118.1
227	201.6	101.8	262	232.7	118.6
228	202.5	102.2	263	233.6	119.0
229	203.4	102.7	264	234.5	119.5
230	204.3	103.2	265	235.4	120.0
231	205.2	103.7	266	236.3	120.5
232	206.1	104.1	267	237.2	121.0
233	207.0	104.6	268	238.1	121.5
234	207.9	105.1	269	238.9	122.0
235	208.7	105.6	270	239.8	122.5
236	209.6	106.0	271	240.7	122.9
237	210.5	106.5	272	241.6	123.4
238	211.4	107.0	273	242.5	123.9
239	212.3	107.5	274	243.4	124.4
240	213.2	108.0	275	244.3	124.9
241	214.1	108.4	276	245.2	125.4
242	215.0	108.9	277	246.1	125.9
243	215.8	109.4	278	246.9	126.4
244	216.7	109.9	279	247.8	126.9
245	217.6	110.4	280	248.7	127.3
246	218.5	110.8	281	249.6	127.8
247	219.4	111.3	282	250.5	128.3
248	220.3	111.8	283	251.4	128.8
249	221.2	112.3	284	252.3	129.3
250	222.1	112.8	285	253.2	129.8
251	223.0	113.2	286	254.0	130.3
252	223.8	113.7	287	254.9	130.8
253	224.7	114.2	288	255.8	131.3
254	225.6	114.7	289	256.7	131.8

¹From Association of Official Agricultural Chemists, "Methods of Analysis," 2d ed. p. 434, 1925.

MUNSON AND WALKER'S TABLE.¹—(Continued)

Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.	Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.
290	257.6	132.3	325	288.7	149.7
291	258.5	132.7	326	289.6	150.2
292	259.4	133.2	327	290.5	150.7
293	260.3	133.7	328	291.4	151.2
294	261.2	134.2	329	292.2	151.7
295	262.0	134.7	330	293.1	152.2
296	262.9	135.2	331	294.0	152.7
297	263.8	135.7	332	294.9	153.2
298	264.7	136.2	333	295.8	153.7
299	265.6	136.7	334	296.7	154.2
300	266.5	137.2	335	297.6	154.7
301	267.4	137.7	336	298.5	155.2
302	268.3	138.2	337	299.3	155.8
303	269.1	138.7	338	300.2	156.3
304	270.0	139.2	339	301.1	156.8
305	270.9	139.7	340	302.0	157.3
306	271.8	140.2	341	302.9	157.8
307	272.7	140.7	342	303.8	158.3
308	273.6	141.2	343	304.7	158.8
309	274.5	141.7	344	305.6	159.3
310	275.4	142.2	345	306.5	159.8
311	276.3	142.7	346	307.3	160.3
312	277.1	143.2	347	308.2	160.8
313	278.0	143.7	348	309.1	161.4
314	278.9	144.2	349	310.0	161.9
315	279.8	144.7	350	310.9	162.4
316	280.7	145.2	351	311.8	162.9
317	281.6	145.7	352	312.7	163.4
318	282.5	146.2	353	313.6	163.9
319	283.4	146.7	354	314.4	164.4
320	284.2	147.2	355	315.3	164.9
321	285.1	147.7	356	316.2	165.4
322	286.0	148.2	357	317.1	166.0
323	286.9	148.7	358	318.0	166.5
324	287.8	149.2	359	318.9	167.0

¹ From Association of Official Agricultural Chemists, "Methods of Analysis," 2d ed. p. 434, 1925.

MUNSON AND WALKER'S TABLE.¹—(Continued)

Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.	Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.
360	319.8	167.5	395	350.9	185.7
361	320.7	168.0	396	351.8	186.2
362	321.6	168.5	397	352.6	186.8
363	322.4	169.0	398	353.5	187.3
364	323.3	169.6	399	354.4	187.8
365	324.2	170.1	400	355.3	188.4
366	325.1	170.6	401	356.2	188.9
367	326.0	171.1	402	357.1	189.4
368	326.9	171.6	403	358.0	189.9
369	327.8	172.1	404	358.9	190.5
370	328.7	172.7	405	359.7	191.0
371	329.5	173.2	406	360.6	191.5
372	330.4	173.7	407	361.5	192.1
373	331.3	174.2	408	362.4	192.6
374	332.2	174.7	409	363.3	193.1
375	333.1	175.3	410	364.2	193.7
376	334.0	175.8	411	365.1	194.2
377	334.9	176.3	412	366.0	194.7
378	335.8	176.8	413	366.9	195.2
379	336.7	177.3	414	367.7	195.8
380	337.5	177.9	415	368.6	196.3
381	338.4	178.4	416	369.5	196.8
382	339.3	178.9	417	370.4	197.4
383	340.2	179.4	418	371.3	197.9
384	341.1	180.0	419	372.2	198.4
385	342.0	180.5	420	373.1	199.0
386	342.9	181.0	421	374.0	199.5
387	343.8	181.5	422	374.8	200.1
388	344.6	182.0	423	375.7	200.6
389	345.5	182.6	424	376.6	201.1
390	346.4	183.1	425	377.5	201.7
391	347.3	183.6	426	378.4	202.2
392	348.2	184.1	427	379.3	202.8
393	349.1	184.7	428	380.2	203.3
394	350.0	185.2	429	381.1	203.8

¹ From Association of Official Agricultural Chemists, "Methods of Analysis," 2d ed. p. 434, 1925.

MUNSON AND WALKER'S TABLE.¹—(Continued)

Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.	Cuprous oxide (Cu ₂ O) Mg.	Copper (Cu) Mg.	Dextrose (d-glucose) Mg.
430	382.0	204.4	460	408.6	220.7
431	382.8	204.9	461	409.5	221.3
432	383.7	205.5	462	410.4	221.8
433	384.6	206.0	463	411.3	222.4
434	385.5	206.5	464	412.2	222.9
435	386.4	207.1	465	413.0	223.5
436	387.3	207.6	466	413.9	224.0
437	388.2	208.2	467	414.8	224.6
438	389.1	208.7	468	415.7	225.1
439	390.0	209.2	469	416.6	225.7
440	390.8	209.8	470	417.5	226.2
441	391.7	210.3	471	418.4	226.8
442	392.6	210.9	472	419.3	227.4
443	393.5	211.4	473	420.2	227.9
444	394.4	212.0	474	421.0	228.5
445	395.3	212.5	475	421.9	229.0
446	396.2	213.1	476	422.8	229.6
447	397.1	213.6	477	423.7	230.1
448	397.9	214.1	478	424.6	230.7
449	398.8	214.7	479	425.5	231.3
450	399.7	215.2	480	426.4	231.8
451	400.6	215.8	481	427.3	232.4
452	401.5	216.3	482	428.1	232.9
453	402.4	216.9	483	429.0	233.5
454	403.3	217.4	484	429.9	234.1
455	404.2	218.0	485	430.8	234.6
456	405.1	218.5	486	431.7	235.2
457	405.9	219.1	487	432.6	235.7
458	406.8	219.6	488	433.5	236.3
459	407.7	220.2	489	434.4	236.9
			490	435.3	237.4

¹ From Association of Official Agricultural Chemists, "Methods of Analysis," 2d ed. p. 434, 1925.

0.4-per cent tannin solution prepared for the determination of soluble matter) is placed in a rectangular cell of 0.5 cm. thickness. White light (preferably daylight) passes through this cell and illuminates one-half of the field that is viewed through the eye-

piece. The other half is illuminated by light that passes through colored glasses. These glasses are colored red, yellow, and blue, and for each color there is provided a series of glasses of differing depths of color, graduated in arbitrary units and tenths of units. Different combinations of glasses are tried until the two halves of the field match. The results are reported as so many units of red, so many of yellow, and so many of blue, or, since red, yellow, and blue make black, and since the blue value is generally small, a number equal to the blue may be subtracted from the red and from the yellow reading, and the result reported simply in terms of yellow and red plus a black value equal to the observed blue value. The higher the reading the greater the depth of color.

The tintometer method has been criticized both on theoretical and on practical grounds (14, 15, 18, 76). Some of the more

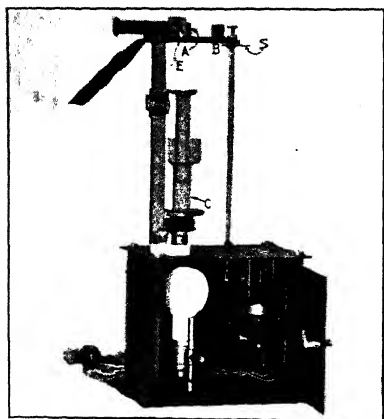


FIG. 72.—Blackadder colorimeter
(Arthur H. Thomas Company).

serious objections are: The glass slides are not sufficiently reproducible; it is possible to get an apparent match with more than one combination of glasses; the results depend very much upon the source of light and, if daylight is employed, upon the clearness of the atmosphere. Moreover, while the measurement is customarily made with the 0.4-per cent tannin solution, the results have always been calculated on the basis of a 0.5-per cent solution, assuming that the color is directly proportional to concentration,

which is not the case (18).

The second method appears to have been suggested by Procter (76) and by Blackadder (14, 15) and worked out by the latter. This method is based upon the fact that the color of any transparent substance is the result of its absorption spectrum. But as it is impractical to determine the absorption spectrum for every wave length, recourse is had to measuring the absorption for four regions of the visible spectrum, which do not overlap, and

which include practically the whole visible spectrum. As worked out by Blackadder, the method consists in measuring the depth of solution of prescribed strength required to absorb just half the light of each of these spectral regions. Results are reported in terms of millimeters of solution for the red, yellow, green, and blue, and, in contrast to the Lovibond method, a high reading means a low intensity of color. Results obtained are independent of the intensity of the light source and of the proportion of different colors of which that light is composed, as long as the whole range of the spectrum is included. Details of the method, for which the authors are indebted to Dr. Blackadder, are given below.

Apparatus.—The Blackadder colorimeter (Fig. 72) is a modification of the original Schmidt and Haensch colorimeter. As shown in the photograph, the instrument is mounted upon a substantial box base that contains a lamp and a motor for rotating the half-light sector. The lamp is mounted in an adjustable holder. Light from this lamp passes by 2 paths to the eye placed at the ocular. By one route the light passes through a rotating sector *S*, which is a disk of which just one-half the area is cut away, permitting just half the light to pass, to the reflecting prism *B*, and so to the eyepiece. By the second route the light passes through the solution in the cup *C*, to the reflecting prism *A*, and thence to the ocular. These prisms *A* and *B* are so arranged that the light passing through the solution illuminates a vertical band across the center of a circle of light thrown by *B*.

The depth of solution traversed by the light is regulated by a hollow plunger of optical glass, worked up and down by a rack and pinion through a vertical distance of 120 mm. The position of the bottom of the plunger is shown by a vertical scale reading directly in millimeters and by means of a vernier to 0.1 mm.

A series of 4 colored glasses is provided. These transmit respectively the red (600 to 700 millimicrons), the yellow (550 to 600 millimicrons), the green (510 to 550 millimicrons), and the blue (400 to 510 millimicrons), portions of the spectrum. One of these screens *E* is placed in front of the telescope, with the result that all the light is filtered out except that of the particular portion of the spectrum selected. The two halves of the field, *i.e.*, the band and the adjacent portions, are of exactly the same color. Thus in making the measurement the eye is called upon to estimate intensity of the light only—not difference in color. This obviates the trouble sometimes encountered in making estimates of color due to non-uniform lighting conditions or partial color blindness.

Setting the Instrument.—Place distilled water in the cup, and gently screw the plunger to its lowest position. The scale should read 0.0 mm. Place the green screen in position, and adjust the lamp so that the illumination is equal in all parts of the field. The sector is not rotated and is set with an open quadrant in the path of the light during this adjustment. The preliminary adjustment is made by means of the adjustable lamp holder,

and the final adjustment by rotating the lamp in its screw socket. Replace the green screen by each of the others in turn; the field should remain evenly illuminated for each color; if not, an adjustment of the lamp must be made for each color in its turn.

Solution.—Prepare a solution of the tanning material containing 0.4 g. of tannin (by the A. L. C. A. method) per 100 cc. (not less than 0.375 nor more than 0.425 g.). Filter as directed under determination of soluble matter.

Procedure.—Empty the cup, rinse once with the tannin solution, and fill the cup to the bottom of the overflow gallery with the plunger raised. Insert the red screen, start the sector rotating, and lower the plunger until the two halves of the field appear equally bright. Record the scale reading to 0.1 mm. Repeat the measurement at least twice, approaching the position of equal illumination from both directions. Take the mean of closely agreeing reading as the "red" value of the liquor. Repeat the determination in turn with the yellow, green, and blue screens in place. If the tannin concentration of the solution is not exactly 0.4 g. per 100 cc., correct the readings by multiplying by the factor $\frac{\text{g. tannin per 100 cc.}}{0.4}$

using the value for tannin found in the determination of tannin according to the A. L. C. A. method.

Report the color of the tanning material in terms of the red, yellow, green, and blue readings of a 0.4-per cent solution.

PLUMPING POWER OF TAN LIQUORS (23, 74, 103)

In being "plumped," a skin absorbs water, its volume increases, and its resistance to compression rises. Resistance to compression is the characteristic property by which plumping is best measured. This is accomplished in the Wilson-Gallun method, described in detail under analysis of lime liquors (Chap. VIII).

Wilson-Gallun Method (103).—Measure the thickness of at least 3 pieces of skin, about 2 cm. square, cut from the butt. For work that is to be of permanent value, these pieces should be prepared as described in Chap. VIII; for comparative tests, skin in the condition obtaining just before tanning may be used. Determine the thickness with a Randall and Stickney gage (Fig. 66), allowing the plunger to rest on the skin for exactly 3 min. Shake the pieces in a stoppered bottle half filled with water to restore their original shape. Place the pieces in the tan liquor, and let stand for 48 hr. Remove the pieces, grasping each by the corner with tweezers, blot them by laying them on filter paper, and redetermine the thickness. Calculate and report plumping power as percentage of increase in thickness or as the ratio of the initial to the final thickness.

AVERAGE COMPOSITION OF TYPICAL TANNING MATERIALS

In Table 44 are collected analytical data for 18 of the commoner tanning materials. With few exceptions, these are extracts.

The tannin composition of raw barks, wood, etc., varies so much with the particular variety, the conditions under which it is grown, age of the plant, season when cut, etc., that analytical data for single samples mean very little. The tannin content of a very large number of plants is tabulated in Wilson's "Chemistry of Leather Manufacture."¹ In all cases except those of valonea and mangrove, the analyses given in Table 44 are the average results for all samples received in the authors' laboratories during the past 10 years. The data for valonea and mangrove have been taken from the annual reports of the Committee on Comparative Tannin Analysis of the A. L. C. A. (77); they represent the compositions of a single sample each. All these data can serve only to indicate in a general way what the result of an analysis of a tanning extract is likely to be.

SYNTANS (20, 27, 28, 32, 33, 42, 47, 81, 90, 93)

When phenol is treated with sulfuric acid, forming phenol-sulfonic acids, and the product is then treated with formaldehyde or other aldehydes, condensation products are formed, some of which are soluble in water and possess tanning properties (102). These products are known as syntans and are marketed under a great number of trade names (Neradol, Leukanol, etc.). While these compounds are not commonly used alone for tanning leather, they are widely used in conjunction with ordinary vegetable tanning materials in tanning and sometimes in connection with the coloring of chrome leather.

The determination of "tannin" in such materials by the official method of the A. L. C. A. gives erratic results, for it is impossible to obtain constant residue weights upon evaporating their solutions to dryness (27, 42). Total and soluble solids may be determined by making the solutions alkaline with sodium hydroxide, correcting for the added alkali. Kohn, Breedis, and Crede (42) attempted to determine the tanning value of syntans by the Wilson-Kern method but found that the hide powder was considerably hydrolyzed by the acid present (it is not clear, however, from their work whether or not they used purified hide powder that had been freed from soluble protein matter). They make the point, which seems well taken, that, as syntans are almost always used in combination with other materials, the proper procedure in examining them is to determine their effects

¹ 2d ed., 1, 392-404.

TABLE 44.—AVERAGE COMPOSITION OF VEGETABLE TANNING MATERIALS

Material	Chestnut extract (liquid)	Cutch extract (solid)	Divi-divi extract (liquid)	Gambier extract (paste)	Gambier extract (cube)	Hemlock bark extract (liquid)	Larch bark extract (liquid)	Larch bark extract (solid)	Myrobolan extract (liquid)	Oak bark extract (liquid)	Osage extract (liquid)	Quebracho extract (solid)	Super spruce extract	Sumac (leaves)	Sumac extract (liquid)	Wattle bark extract (solid)	Yaloua (cups and beards)	Manrove bark
Specific gravity at 60°F., Barkometer reading of solution containing 1 lb. per gallon.....	1.218	1.207	1.220	1.220	1.220	1.220	1.220	1.101	1.215	1.226	1.254	1.232						
Water.....	24	30	21	22	23	43	21½	22	23	31	26	22	24	38	17.04	9.00	11.57	
Total solids.....	57.53	21.52	60.57	51.72	14.23	25.70	9.12	61.65	54.07	49.78	22.60	49.07	9.00	54.84	90.10	45.16	82.06	47.68*
Matter insoluble at 70°F. Soluble matter.....	42.47	78.48	39.43	48.28	85.77	46.76	47.30	90.88	38.35	45.93	50.22	77.40	50.93	90.10	45.16	82.06	47.68*	61.41*
Soluble non-tannin.....	41.06	70.86	30.57	41.08	76.67	40.99	43.40	88.76	37.97	43.13	46.01	69.90	50.24	44.46	42.90	80.28	45.06	60.27
Tannin (A. L. C. A. method).....	13.77	20.00	13.94	15.37	35.84	15.74	19.44	88.98	43.19	18.54	11.31	7.06	25.34	19.15	18.99	17.21	14.57	11.33
Total sugars as glucose... Sulfate as trioxide..... Chlorides as chlorine..... Total ash..... Ash of soluble matter..... Sodium carbonate..... Iron and aluminum (oxides)..... Calcium as oxide..... Magnesium as oxide..... pH value of solution con- taining 4 g. of tannin per liter.....	27.29 4.93 Trace 0.08 0.61 1.12 0.47 0.43 5.23	56.86 1.51 4.55 0.20 1.47 4.45 0.07 0.47 0.43	22.03 4.01 0.20 0.27 1.41 0.57 Trace 0.11 Trace	25.71 7.94 0.46 0.47 3.06 5.58 1.74 0.83 0.21 0.02 0.14 4.63	25.25 5.27 Trace 0.07 1.08 0.96 0.77 25.24 0.17 Trace 0.54 3.77	24.05 7.28 Trace 0.21 1.74 1.43 0.80 24.05 0.12 Trace Trace 3.94	49.72 17.08 1.03 0.72 3.74 3.53 1.13 49.72 0.20 0.33 0.15 4.50	24.78 3.94 Trace 0.18 1.58 1.13 24.78	24.57 6.01 5.00 0.30 1.70 1.50 0.50 24.57 0.08 0.32 0.14 4.36	34.70 1.22 0.09 0.28 2.32 34.70 5.00	62.84 1.22 Trace 0.30 1.70 0.51 0.22 62.84 Trace 0.19 0.06 4.77	24.90 9.82 6.66 0.54 3.73 3.62 2.87 24.90 0.05 0.20 1.58 2.86	25.31 3.06 0.64 0.52 8.25 2.98 1.25 25.31 0.13 0.29 0.27 4.02	23.91 0.36 0.36 0.69 2.77 1.64 1.33 23.91 0.04 0.20 0.28 4.14	63.07 4.47 0.14 0.85 1.77 1.60 63.07 0.06 0.17 0.17 5.03	30.49 30.49		

* Found in analytical solution.

on tannin fixation from solutions similar to the liquors actually used. Such a study was made for one syntan with two vegetable tanning materials by Thomas and Kelly (93).

Attempts have been made to distinguish between free sulfuric acid and sulfonic acid in syntans. Such attempts have been shown to be futile (42), since an equilibrium exists between these acids, which is disturbed by any attempt to remove and determine either one of them. The significant characteristics of syntans or their solutions are pH value and total acidity. The pH value determinations cannot be made with the hydrogen electrode, due to poisoning of the electrode (Chap. VII) but can be made with the quinhydrone electrode. Total acidity (95) is determined by titration, using phenolphthalein indicator. Kohn, Breedis, and Crede (42) recommend a test designed to determine whether or not syntans have the "correct" acidity. This test consists in determining the completeness of detannization of a syntan solution by hide powder and the reaction of the solution toward methyl orange. When the acidity is too low, the syntan solution cannot be detannized by hide powder, and the solution, after shaking with hide powder, responds to the gelatin-salt test. If the acidity is too high, the solution is completely detannized but reacts acid toward methyl orange. At the correct acidity detannization is complete, and the solution reacts neutral or very slightly acid toward methyl orange.

Ash, composition of ash, total sulfur, and total chloride in syntans may be determined as in vegetable tannins.

References

1. AMERICAN LEATHER CHEMISTS ASSOCIATION: "Methods of Analysis," pub. by the secretary, New York.
2. AMERICAN LEATHER CHEMISTS ASSOCIATION: Official International Method of Quantitative Tannin Analysis, *J. Am. Leather Chem. Assoc.*, **22**, 311, 1927.
3. AMERICAN LEATHER CHEMISTS ASSOCIATION: Revision of Official Method for Sampling Tanning Materials, *ibid.*, **22**, 452, 1927.
4. ANACKER, E.: Evaluation of Cellulose Extracts, *Collogium*, 495, 1928.
5. ATKIN, W. R.: Effects of Varying Hydrogen-ion Concentration on Tannin Analysis, *J. Am. Leather Chem. Assoc.*, **19**, 442-446, 1924.
6. ATKIN, W. R., and F. C. THOMPSON: Determination and Control of Acidity in Tan Liquor, *J. Soc. Leather Trades Chem.*, **4**, 143, 1920; *J. Am. Leather Chem. Assoc.*, **16**, 9-20, 1921.
7. ATKIN, W. R., and F. C. THOMPSON: Hide Powder, *J. Intern. Soc. Leather Trades Chem.*, **11**, 300, 1927.

8. BALDRACCO, G.: Note on the Modified Shake Method, *Cuir tech.*, **15**, 99, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 360, 1926.

9. BALDRACCO, G.: Modified Agitation Method for Analysis of Tannins, and the Darmstadt Apparatus, *J. Intern. Soc. Leather Trades Chem.*, **13**, 365-375, 1929.

10. BALDRACCO, G., and S. CAMILLA: Note on the Modified Shake Method for the Determination of Non-tans, *Cuir*, **13**, 73, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 545, 1924.

11. BEANS, H. T., and E. LITTLE: Study of the A. L. C. A. Official Method for the Determination of the Acidity of a Tan Liquor, *Ind. Eng. Chem.*, **17**, 252, 1925; Use of the Cadmium Half Cell for the Determination of Acidity of a Tan Liquor, *ibid.*, **17**, 413, 1925.

12. BENNETT, H. G.: Acidity of Tan Liquors, *Collegium*, London ed. 106-113, 1916; *J. Am. Leather Chem. Assoc.*, **11**, 500-510, 1916.

13. BENNETT, H. G.: Methods of Testing Hide Power, *Collegium*, London ed. 155-160, 1916; *J. Am. Leather Chem. Assoc.*, **12**, 22-29, 1917; Standardization of Hide Powder: II, and III., *J. Intern. Soc. Leather Trades Chem.*, **10**, 355, 1926; **11**, 87, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 484, 652, 1927.

14. BLACKADDER, T., et. al.: Color Measurement of Tanning Materials, *J. Soc. Leather Trades Chem.*, **7**, 445, 1923; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 209, 1924; Color Measurement of Tanning Solutions, Committee Reports; *J. Am. Leather Chem. Assoc.*, **16**, 280-283, 1921; **17**, 206-210, 1922; **18**, 438-440, 1923; Practical Method of Color Measurement, *ibid.*, **18**, 194-201, 1923.

15. BLACKADDER, T. and C. E. GARLAND: Need of a Standard Method for Color Determination, *J. Am. Leather Chem. Assoc.*, **15**, 181-186, 1920.

16. BRIGGS, R. P.: Quantitative Differentiation between Cube Gambier and Indian Cutch, *Analyst*, 379, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 121, 1925.

17. BROWN, R. J.: Ultrafiltration of Tannin and Other Solutions, *J. Soc. Leather Trades Chem.*, **7**, 365, 1923; **10**, 235, 1926.

18. BRUERE, A. DE LA: Measurement of Color of Tanning Extracts, *Cuir tech.*, **17**, 342-345, 1928.

19. BRUERE, A. DE LA: Spectrophotometry of Tanning Extracts in the Ultra-violet, and pH, *Cuir tech.*, **14**, 266, 351, 1925; *J. Am. Leather Chem. Assoc.*, **21**, 47, 184, 1926.

20. BRUERE, A. DE LA: Synthetic Tannins: Absorption Spectra in the Ultra-violet and Precipitation Reactions, *Cuir*, **13**, 393, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 38, 1925.

21. CAMERON, D. H.: Improved Steam Still for Volatile Acids (in Tan Liquors), *J. Am. Leather Chem. Assoc.*, **23**, 42-45, 1928.

22. CASTE, M.: Determination of Insoluble Matter in Tanning Liquors by Centrifugation, *Cuir tech.*, **14**, 183, 1925; *J. Soc. Leather Trades Chem.*, **9**, 217, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 390, 1925.

23. CLAFLIN, A. A., et al.: Measurement of Plumping Power of Solutions, *J. Am. Leather Chem. Assoc.*, **15**, 234-241, 1920; Measurement of Plumping by Claffin's Method, Committee Report, *ibid.*, **16**, 562-578, 1921.

24. CLARK, I. D., and R. W. FREY: Determination of Sugars in Tanning Extracts, *J. Am. Leather Chem. Assoc.*, **23**, 91-108, 1928.

25. CREDE, E.: Astringency of Vegetable Tan Liquors, *ibid.*, **20**, 573-576, 1925.
26. DOWNING, G. V.: Alternate Filter Papers, Committee Report, *ibid.*, **19**, 398-404, 1924.
27. ESCOURROU, R.: Determination of Syntans, *Halle aux Cuirs*, 77-81, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 493, 1927.
28. FAUST, T. A., et al.: Analysis of Synthetic Tanning Materials, Committee Report, *J. Am. Leather Chem. Assoc.*, **17**, 622-638, 1922.
29. FREY, R. W.: Kaolin for Tannin Analysis, *ibid.*, **14**, 393-401, 1919.
30. FREY, R. W., and I. D. CLARK: Rapid Washing of Chromed Hide Powder, *ibid.*, **16**, 477-480, 1921.
31. FREY, R. W., and H. C. REED: Practical Glass Extractor for Tanning Materials, *ibid.*, **23**, 124-128, 1928.
32. GERNGROSS, O.: Employment of Filtered Ultra-violet Light for Detection and Differentiation of Artificial and Natural Tanning Materials, *Gerber*, 213, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 246, 1927.
33. GERNGROSS, O., and G. SANDOR: Fluorescence Test: The Fluorescence of Natural Tanning Extracts in Ultra-violet Light, II., *Collegium*, 1, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 297, 1927.
34. HARVEY, A.: "Practical Leather Chemistry," Crosby, Lockwood, and Son, London, 1920.
35. HOUGH, A. T.: Determination of Bisulfites in Extracts, *Cuir*, **9**, 162-163, 1920.
36. HUGONIN, G.: Determination of Insoluble Matter by Centrifugation. Unification of the Acidity of Tanning Solutions, *Cuir*, **12**, 510, 1923; Influence of Acidification of Tanning Solutions upon the Unification of the Absorption Coefficients of Different Hide Powders, *ibid.*, **13**, 22, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 217, 1924.
37. HUGONIN, G.: Quantitative Tannin Analysis, Committee Reports, *Cuir*, **12**, 328, 1923; *ibid.*, **13**, 436, 539, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 296, 300, 1925.
38. INTERNATIONAL SOCIETY OF LEATHER TRADES CHEMISTS: Official Method of Tannin Analysis, *J. Intern. Soc. Leather Trades Chem.*, **10**, 30, 1926; *J. Am. Leather Chem. Assoc.*, **21**, 308-320, 1926.
39. JAMET, A., and A. GIRARD: Determination of Insolubles by Filtration in the Presence of Kaolin, *Cuir tech.*, **17**, 346, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, **23**, 587, 1928.
40. KERN, E. J., and J. W. KOENIG: Acidity of Vegetable Tan Liquors, *Ind. Eng. Chem.*, **16**, 261, 1924.
41. KNOWLES, G. E.: Effect of Adjusting pH Value in Tannin Analysis, *J. Soc. Leather Trades Chem.*, **7**, 437, 1923.
42. KOHN, S., J. BREEDIS, and E. CREDE: Determination of Active Constituent of Synthetic Tanning Materials, *J. Am. Leather Chem. Assoc.*, **17**, 166-180, 1922; Acidity of Synthetic Tans, *ibid.*, **18**, 21-24, 1923.
43. KUBELKA, V.: Tannin Determination by the Shake Method with the Assistance of the Centrifuge; *Collegium*, 21, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 151, 1929.
44. KUBELKA, V., and E. BELAVSKY: Definition and Method for Determining So-called Insolubles in Tanning Extracts: II. and III., *Collegium*, 111, 247, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 43, 479, 1926.

45. KUBELKA, V., and J. WAGNER: Determination of Acid Content of Tan Liquors, *Collegium*, 41, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, 19, 750, 1924.
46. LAUFFMANN, R.: Method of Determination of Acetyl Absorption of Tanning Extracts and Other Materials and the Use of Acetylated Tanning Materials for Their Differentiation and Testing, *Collegium*, 370, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, 21, 532, 1926.
47. LAUFFMANN, R.: Test for Synthetic Tannins, *Collegium*, 169-171, 1920; abstracted in *J. Am. Leather Chem. Assoc.*, 16, 50, 1921.
48. LEVI, L. E., and E. V. MANUEL: "Tanners' and Chemists' Handbook," Privately printed, Milwaukee, Wis., 1909.
49. LEVI, L. E., and A. C. ORTHMANN: "Laboratory Manual," The Pfister and Vogel Leather Co., Milwaukee, Wis., 1918.
50. LITTLE, E., and H. T. BEANS: Use of Hide Powder as a Detanning Agent in the Determination of the Acidity of a Tan Liquor, *J. Am. Leather Chem. Assoc.*, 20, 103-120, 1925.
51. LONGBOTTOM, H. L.: Estimation of Reducing Sugars in Tannin Solutions of Analytical Strength, *ibid.*, 17, 104-109, 1922.
52. MARSHALL, F. F.: Rapid Washing of Chromed Hide Powder, *ibid.*, 17, 210-217, 1922.
53. McCANDLISH, D., and W. R. ATKIN: The Detanning Process of Tannin Analysis, *J. Soc. Leather Trades Chem.*, 9, 161, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, 20, 486, 1925.
54. McCANDLISH, D., and W. R. ATKIN: Determination of Insolubles in Tannin Solutions, *J. Am. Leather Chem. Assoc.*, 24, 231-235, 1929.
55. MERRILL, H. B., et. al.: Determination of Moisture in Tanning Extracts, Committee Report, *J. Am. Leather Chem. Assoc.*, 24, 314-321, 1929.
56. MERRILL, H. B.: Control Methods for Tan Liquors Used for Tanning Light Leathers, *J. Am. Leather Chem. Assoc.*, 24, 663, 1929.
57. MEUNIER, L., P. CHAMBARD, and A. JAMET: Preparation of Hide Powder to be Used in Analysis, *Cuir tech.*, 13, 518, 1924; 14, 178, 1925; 14, 458, 1925; *J. Soc. Leather Trades Chem.*, 9, 23, 1925; 9, 200, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, 20, 299, 390, 1925; 21, 185, 1926.
58. MEUNIER, L., and A. JAMET: Fluorescence of Sulfite Cellulose Extracts and Its Applications, *Cuir tech.*, 15, 166, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, 21, 361, 1926.
59. MEUNIER, L., and A. JAMET: Problem of the Industrial Determination of Tannin, *Cuir tech.*, 15, 218, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, 21, 478, 1926.
60. MEZEY, E.: Definition and Determination of the Astringency of Vegetable Tanning Materials, *Cuir tech.*, 14, 195, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, 20, 618, 1925.
61. PAESSLER, J.: The New (International) Method of Tannin Analysis, *Collegium*, 352-361, 1928.
62. PARKER, J. G.: Darmstadt Apparatus for Tannin Analysis, *J. Intern. Soc. Leather Trades Chem.*, 12, 520, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, 24, 326, 1929.

63. PARKER, J. G.: Extraction of Solid Tanning Materials by the Koch and Procter Apparatus under Identical Conditions, *J. Intern. Soc. Leather Trades Chem.*, **12**, 564, 1928; *J. Am. Leather Chem. Assoc.*, **23**, 590-595, 1928.
64. PARKER, J. G.: Improved Tintometer, *J. Intern. Soc. Leather Trades Chem.*, **12**, 417, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 217, 1929.
65. PARKER, J. G.: Tannin Analysis, Committee Report, *J. Intern. Soc. Leather Trades Chem.*, **13**, 412-421, 1929.
66. PARKER, J. G., and J. T. TERRELL: Insolubles in Tannin Solutions, *J. Intern. Soc. Leather Trades Chem.*, **11**, 196, 1927; *J. Am. Leather Chem. Assoc.*, **22**, 655, 1927.
67. PARKER, J. G., and J. T. TERRELL: Tests with Various Hide Powders Using Buffer Solutions of pH = 4.6, *J. Intern. Soc. Leather Trades Chem.*, **9**, 479, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 225, 1926.
68. PARKER, J. G., and L. WINCH: Extraction of Sumac for Analysis, *J. Intern. Soc. Leather Trades Chem.*, **10**, 272, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 111, 1927.
69. PHILLIPS, R. O.: Determination of Astringency and Penetration Value of Tan Liquors, *J. Am. Leather Chem. Assoc.*, **17**, 565, 1922.
70. PHILLIPS, R. O.: Importance of Better Standardization: I. Hide Powder, *ibid.*, **19**, 732-736, 1924; II. Kaolin, *ibid.*, **19**, 742-744, 1924.
71. PILGRIM, J. A.: The Official Method and the Filtration of Tanning Material Infusions in Tropical Countries, *J. Soc. Leather Trades Chem.*, **7**, 467, 1923; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 212, 1924.
72. POLLAK, J., and W. SPRINGER: Recognition of Quebracho and Similar Tanning Materials in Extract Mixtures and in Leather, *Gerber*, **87**, 93, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, **23**, 71, 1928.
73. POLLAK, L.: Detection of Sulfite Cellulose Extract in Tanning Extracts, *Gerber*, **53**, 1927.
74. PORTER, R. E., et al.: Direct Measurement of the Plumping Power of Tan Liquors, Committee Reports, *J. Am. Leather Chem. Assoc.*, **19**, 354-362, 1924; **20**, 282-293, 1925; **21**, 425-435, 1926; **22**, 521-525, 1927.
75. PROCTER, H. R.: "Leather Chemists' Pocket Book." R. & E. N. Spon, London, 1912; Leather Industries Laboratory Book, R. & E. N. Spon, London, 1908.
76. PROCTER, H. R.: Measurement of Color of Brown Solutions with Special Reference to Tannin Extracts, *J. Soc. Chem. Ind.*, **42**, 73-79, 1923; abstracted in *J. Am. Leather Chem. Assoc.*, **18**, 447, 1923.
77. REED, H. C.: Comparative Analysis of Tanning Materials, Committee Reports, *J. Am. Leather Chem. Assoc.*, **17**, 256-262, 1922; **19**, 243-257, 1924; **20**, 205-206, 1925; **21**, 302-306, 1926.
78. REED, H. C.: Preparation of Fresh Tanning Materials for Analysis, *J. Am. Leather Chem. Assoc.*, **16**, 620, 1921.
79. RIESS, C.: Determination of Insoluble Matter in Tanning Extracts, *J. Am. Leather Chem. Assoc.*, **24**, 229-231, 1929.
80. ROGERS, J. S., et al.: Effect of Definite Hydrogen-ion Concentration upon Analysis of Tanning Extracts by the Official Method, Committee Reports, *ibid.*, **19**, 314-335, 1924; **20**, 370-373, 1925.

81. ROHM & HAAS Co.: Synthetic Tans (Chemical Examination), *ibid.*, 19, 118-119, 1924.
82. SCHELL, E.: Observations on Baldracco and Camilla's Modification of the Method for Detannization, *Cuir*, 12, 470, 1923.
83. SCHULTZ, G. W.: Study of the Processes Involved in Tannin Analysis, Part I, *J. Am. Leather Chem. Assoc.*, 18, 524, 1923.
84. SCHULTZ, G. W.: The Wilson-Kern Method of Tannin Analysis, *ibid.*, 16, 349-367 and 637-641, 1921.
85. SCHULTZ, G. W., and T. BLACKADDER: Observations on the Determination of True Tanning Value of Extracts According to Wilson and Kern, *ibid.*, 15, 654-664, 1920.
86. SHEARD, L.: Improved Extractor for Extraction of Tanning Materials for Analysis, *J. Soc. Leather Trades Chem.*, 8, 223, 1924.
87. SIMONCINI, E.: Acidity of Tan Liquors, *Boll. Ufficiale staz. sper. ind. pelli mat. concieri*, 1, 26, 1923; abstracted in *J. Am. Leather Chem. Assoc.*, 19, 685, 1924.
88. SMOOT, C. C., III. The Blackadder Colorimeter, *J. Am. Leather Chem. Assoc.*, 19, 571-573, 1924.
89. STIASNY, E.: Darmstadt Apparatus for Tannin Analysis, *Collegium*, 383-388, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, 24, 389-390, 1929.
90. STIASNY, E., ed.: "Gerbereitechnisches Taschenbuch," 2d ed., Theodor Steinkopff, Dresden and Leipzig, 1929.
91. STIASNY, E.: Qualitative Tannin Analysis (Summary of the Literature, 1925 to 1927), *Collegium*, 184, 1927.
92. THOMAS, A. W., and A. FRIEDEN: The Gelatin-tannin Reaction, *Ind. Eng. Chem.*, 15, 839, 1923.
93. THOMAS, A. W., and M. W. KELLY: Syntan Tannage, *ibid.*, 21, 698, 1929.
94. THOMAS, A. W., and M. W. KELLY: Ultra-filtration of Vegetable Tanning Solutions, *ibid.*, 18, 136, 1926.
95. THOMPSON, F. C.: Hide Powder, *Leather Trades Year Book*, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, 21, 221, 1926.
96. THOMPSON, F. C., and W. R. ATKIN: Hide Powder and Tannin Analysis, Committee Reports, *J. Soc. Leather Trades Chem.*, 9, 157, 1925; 9, 405, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, 20, 608, 1925.
97. THOMPSON, F. C., K. SESHACHALAM, and K. HASSAN: Influence of Degree of Acidity on Tannin Content of Solutions, *J. Soc. Leather Trades Chem.*, 5, 389, 1921.
98. THUAU, U. J., and L. FAYRE: Role of Sulfuricinoleate (Soluble Castor Oil) in the Official Method of Tannin Analysis, *Cuir*, 13, 118, 1924.
99. TURNBULL, A.: New Method for the Determination of Insolubles in Tanning Extracts, *J. Am. Leather Chem. Assoc.*, 23, 224-225, 1928.
100. WARE, A. H.: An Apparently Specific Test for Tannin, *Analyst*, 467-471, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, 20, 123, 1925.
101. WILLIAMS, H. E.: Extraction of Tanning Materials Using a Modified Teas Extractor, *J. Am. Leather Chem. Assoc.*, 22, 97-102, 1927.
102. WILSON, J. A.: "The Chemistry of Leather Manufacture," 2d ed., vol. I, A. C. S. Mon. Ser., The Chemical Catalog Company, Inc., New York, 1928.

VEGETABLE TANNING MATERIALS

103. WILSON, J. A., and A. F. GALLUN, JR.: Direct Determination of the Plumping Power of Tan Liquors, *Ind. Eng. Chem.*, **15**, 376, 1923.

104. WILSON, J. A., and E. J. KERN: Color Value of a Tan Liquor as a Function of Hydrogen-ion Concentration, *ibid.*, **13**, 1025, 1921.

105. WILSON, J. A., and E. J. KERN: True Tanning Value of Vegetable Tanning Materials, *Ind. Eng. Chem.*, **12**, 465, 1920; *J. Am. Leather Chem. Assoc.*, **15**, 295-308, 1920; Nature of the Hide-tannin Compound and Its Bearing on Analysis, *Ind. Eng. Chem.*, **12**, 1,149, 1920; *J. Am. Leather Chem. Assoc.*, **16**, 75-85, 1921; Determination of Tannin, *Ind. Eng. Chem.*, **13**, 772, 1921; *J. Am. Leather Chem. Assoc.*, **16**, 622-631, 1921; The Wilson-Kern Method of Tannin Analysis—A Reply, *J. Am. Leather Chem. Assoc.*, **16**, 631-637, 1921.

106. WILSON, J. A., and E. J. KERN: Effect of Hydrogen-ion Concentration on Analysis of Vegetable Tanning Materials, *Ind. Eng. Chem.*, **14**, 1,128, 1922.

CHAPTER X

CHROME TANNING MATERIALS AND LIQUORS

Besides compounds of chromium, a considerable number of accessory materials are required in tanning skins with chromium. To bring the skins into the proper conditions for tanning (44), they are generally pickled with dilute acid, to which salt is added. The tanning operation proper may be carried out either by the two-bath or the one-bath process. In the two-bath process the skins are treated first with a solution of sodium dichromate, followed by an acid solution of a reducing agent, usually sodium thiosulfate, which reduces the chromate to a chromic salt. In the one-bath process chromic salts are applied to the skin directly. The compound in most common use is the basic sulfate, although chlorides have been used and complex chromiates have been suggested. These salts are manufactured by reducing the bichromate in acid solution, just as is done in the two-bath process, except that cheaper reducing agents are used instead of thiosulfate. The most important reducing agents used in making chromic compounds are sulfur dioxide, sulfites and a wide variety of cheap organic substances. After the skins have been treated with chromium compounds, they must be neutralized partially. This is done with sodium bicarbonate or carbonate, borax, disodium phosphate, or other mildly alkaline compound, either added to the partially exhausted chrome liquor or applied as a separate bath after the skins have been removed from the chrome liquor.

Aluminum and iron compounds possess tanning properties similar to these possessed by chromic salts and are sometimes used for tanning, either alone or in conjunction with chromium. The most important aluminum compounds so used are aluminum sulfate and ordinary alum. These substances are also used elsewhere in the tannery, particularly as mordants in coloring. Iron compounds have not been used extensively except in Germany during the war-time shortage of chromium, and the exact nature of the compounds used has not been divulged.

This chapter deals with the analysis of chrome and aluminum tanning compounds and chrome liquors, pickle liquors, and acids used in pickling, reducing agents, and neutralizing agents.

CHROMIUM SULFATE (BASIC CHROMIUM SULFATE, CHROME ALUM)

Basic chromium sulfate, the most widely used chrome tanning compound, is manufactured by reducing sodium bichromate with sulfur dioxide, sulfites, thiosulfates, glucose, sawdust, or other organic matter, in acid solution. The quantity of acid present is generally insufficient to saturate all the primary valences of the chromium, resulting in the formation of a basic salt. After reduction, the solution is evaporated to a thick syrup, which solidifies on cooling. The product therefore contains the by-products of the reduction, principally sodium sulfate, as well as the impurities present in the bichromate or the chromite ore from which the latter was prepared, including considerable aluminum and smaller amounts of iron.

Pure, neutral chromium sulfate and chrome alum (the double sulfate of sodium or potassium and chromium) are analyzed by the same methods as the basic sulfate.

The analysis of chromium sulfate includes the determination of chromium, aluminum, iron, neutral sulfate as sodium sulfate, "acid" sulfate (sulfate combined with chromium, aluminum, and iron), acidity of the chromium salt, and chlorides. Samples of basic chromium sulfate analyzed in the authors' laboratory during the past 10 years have had the following average composition: chromium (chromic oxide), 23.47 per cent; aluminum (as oxide), 2.59 per cent; iron (ferric oxide), 0.42 per cent; acid sulfate (as sulfur trioxide), 26.07 per cent; neutral sulfate (as sodium sulfate), 30.53 per cent; chlorides (as sodium chloride), 1.26 per cent; acidity of the chromium-iron-aluminum salt, 0.52.

Preparation of Sample.—Basic chromium sulfate is generally marketed as a fine, dark green powder. If the sample contains lumps or crystals, grind thoroughly until the entire sample passes a screen of 80 meshes to the inch. Mix, and preserve in a well-stoppered glass container.

Insoluble Matter.—Weigh accurately about 10 g. into a 400-cc. beaker. Add 100 cc. of cold water, stir well, and allow to stand overnight. Add 200 cc. more water, and boil until solution is apparently complete. Filter, and wash with hot water until the washings are free from sulfate.

Examine the filter paper for evidence of the presence of carbon. This is indicated by a gray to black discoloration of the paper.

Ignite the filter paper and residue in a weighed platinum dish, cool in a desiccator, and weigh. Calculate and report percentage of insoluble matter. If the percentage found exceeds 0.5, analyze it as directed under analysis of ash of chrome leather (Chap. II).

Chromium (16, 17, 22, 23, 28, 32, 34, 35, 36, 37, 40).—Weigh accurately about 0.25 g. into a 250-cc. Erlenmeyer flask, treat with 100 cc. of water and about 2 cc. of concentrated hydrochloric acid, and heat to boiling. Cool the solution, and add cautiously, in small increments, about 2 g. of pure, iron-free sodium peroxide. Place a small short-stemmed funnel in the mouth of the flask to act as a reflux condenser, heat to boiling, and boil gently for 1 hr., replacing the water lost by evaporation. Cool the solution under the tap. Filter the solution and wash the filter three times with hot water. Preserve the filtrate and washings. Dissolve the precipitate (principally iron hydroxide) by pouring hot, dilute hydrochloric acid on the filter, catch the solution in the flask previously used, and wash the paper until it is free from chlorides. Treat the solution with sodium peroxide and boil as before. Filter, combining the filtrate with the first one, and wash the paper free from chlorides. Concentrate the combined filtrate and washings to a volume of about 100 cc. Cool the solution to room temperature, add 15 cc. of concentrated hydrochloric acid, and cool again. Add 10 cc. of 10-per cent potassium iodide solution. Titrate with recently standardized, approximately tenth-normal sodium thiosulfate solution, until the green color of reduced chromium begins to predominate over the brown color of free iodine. Then add 1 or 2 cc. of starch indicator and add more thiosulfate dropwise until the dark blue color changes to a clear sea green. Take the first disappearance of the blue as the end point, and ignore any return of the blue (due to air oxidation). Calculate and report percentage of chromic oxide.

$$\text{Per cent Cr}_2\text{O}_3 = \frac{\text{cc. approx. } 0.1\text{-}N \text{ Na}_2\text{S}_2\text{O}_3 \times \text{factor} \times 0.2533}{\text{g. sample weighed}}$$

NOTE.—By this procedure, any chromium present in a form insoluble in dilute hydrochloric acid will not be included. The method determines, however, all chromium available for tanning.

Iron (22, 36, 37).—Weigh accurately about 2 g. into a 400-cc. beaker, treat with 100 cc. of water and a few centimeters of concentrated hydrochloric acid, and boil until solution is complete. Cool to room temperature. Add cautiously, in small increments, enough sodium peroxide (free from aluminum and iron) to make the solution strongly alkaline, and boil until the solution assumes a clear yellow color. Cool, filter, and wash until the paper is colorless. Save the filtrate and washings for the determination of aluminum. Treat the precipitate with warm, dilute hydrochloric acid, taking care not to break the filter, and wash the paper free from chlorides. Reprecipitate iron as hydroxide with ammonia, boil until the excess ammonia is expelled, cool, filter, and wash the precipitate free from chlorides. Ignite the paper and precipitate in a weighed crucible, cool in a desiccator, and weigh. Calculate and report percentage of iron as oxide.

$$\text{Per cent Fe}_2\text{O}_3 = \frac{\text{g. sample weighed}}{\text{g. sample weighed}}$$

Aluminum (37).—Combine the two filtrates from the precipitation of iron. Acidify the solution with dilute hydrochloric acid, and heat to boiling. Add dilute ammonia slowly until the solution is just alkaline, then boil until the odor of ammonia can no longer be detected. Filter, and wash two or three times with hot water. Treat the precipitate with warm, dilute hydrochloric acid catch the filtrate in the beaker used for the original precipitation, and wash the paper free from chlorides. Reprecipitate with ammonia as before, filter, and wash the precipitate free from chlorides. Ignite the paper and precipitate in a weighed crucible, cool in a desiccator, and weigh. Calculate and report percentage of aluminum as oxide.

$$\text{Per cent Al}_2\text{O}_3 = \frac{\text{g. Al}_2\text{O}_3}{\text{g. sample weighed}} \times 100$$

"Acid" Sulfate (33, 41).—By acid sulfate is meant sulfate so combined as to be easily hydrolyzable as sulfuric acid.

Weigh accurately about 0.5 g. into a 1,000-cc. porcelain casserole. Add about 600 cc. of recently boiled distilled water, and heat to boiling. Add 5 drops of phenolphthalein indicator, and titrate the hot solution with tenth-normal sodium hydroxide until the indicator turns pink. Cover the solution with a watch glass, replace the casserole over the flame, and boil for 1 min. If the color is discharged, add more tenth-normal sodium hydroxide until the color is restored, and boil again. Repeat until the color is not discharged upon boiling for 1 min. Calculate and report percentage of acid sulfate as sulfur trioxide.

$$\text{Per cent acid SO}_3 = \frac{\text{cc. } 0.1\text{-N NaOH} \times 0.4}{\text{g. sample weighed}}$$

NOTE.—Exclude carbon dioxide by the use of a watch glass, as directed, and carry out the titration as rapidly as possible.

Electrometric Method.—This method, described by Thomas (41), is less convenient than the titration with phenolphthalein but probably more accurate. For the determination, an outfit for determining *conductance* (not a potentiometer) is required. The solution of chromic sulfate is placed in a conductivity cell and titrated with tenth-normal barium hydroxide until the conductivity passes through a minimum which is taken as the end point. The method depends upon the fact that when sulfate combined with chromium is precipitated as barium sulfate, chromic hydroxide is likewise precipitated, and the conductance falls, while precipitation of sulfate combined with sodium results in the formation of an equivalent amount of sodium hydroxide, and the conductance increases. For details, Thomas' original paper should be consulted.

Neutral Sulfate.—Weigh accurately about 0.5 g. into a 400-cc. beaker, treat with 250 cc. of water and 10 cc. of strong hydrochloric acid and boil. Filter if necessary to remove insoluble matter, and wash the paper free from chlorides with hot water. Heat the filtrate to boiling, and add, drop by drop, with stirring, about 10 cc. of 10-per cent barium chloride solution. Let the precipitate stand overnight. Filter through Whatman No. 44 paper or its equivalent, and wash twice with dilute hydrochloric acid and then with water until the washings are free from chlorides. Ignite in a tared platinum crucible, heating gently until the paper is decomposed, then gradually increasing to the maximum temperature of an ordinary Bunsen burner. Cool in a desiccator, and weigh as barium sulfate.

If the barium sulfate is greenish, due to absorbed chromium, add several grams of sodium carbonate to the residue, and fuse at bright red heat. Cool, and extract the fusion with hot water, filter, and wash the insoluble barium carbonate free from sulfate. Make the filtrate acid with hydrochloric acid, and reprecipitate barium sulfate as described above.

Calculate percentage of total sulfate as sulfur trioxide. Subtract percentage of acid sulfate as sulfur trioxide, and calculate the difference as percentage of sodium sulfate.

$$\text{Per cent total SO}_3 = \frac{\text{g. BaSO}_4 \times 34.3}{\text{g. sample weighed}}$$

$$\text{Per cent Na}_2\text{SO}_4 = (\text{per cent total SO}_3 - \text{per cent acid SO}_3) \times 1.774$$

Chlorides.—Weigh accurately about 2 g. into a 500-cc. porcelain casserole. Add about 100 cc. of water, heat to boiling, and add normal sodium hydroxide, drop by drop, until the solution is alkaline to phenolphthalein, then make slightly acid with acetic acid. Add a few drops of a 10-per cent solution of potassium chromate. Titrate with tenth-normal silver nitrate, added drop by drop, until a permanent brick-red precipitate is formed. Calculate and report as percentage of sodium chloride.

$$\text{Per cent NaCl} = \frac{.01-N \text{ AgNO}_3 \times 0.584}{\text{g. sample weighed}}$$

NOTE.—By the methods here given, all the acid (hydrolyzable) anion is considered to be sulfate, and all the chloride is considered bound as neutral chloride. This is purely arbitrary, but it is impossible to determine the distribution of chloride and sulfate between chromium and sodium, in a substance containing all four ions, and some arbitrary rule must be followed in order to secure consistency in reporting results.

Acidity of Chromium Salt.—Using the values for percentages of acid sulfate, chromic oxide, aluminum oxide, and ferric oxide obtained in the preceding determinations, calculate percentage of acidity by means of the equation

$$\text{Acidity}^1 = \left(\frac{\text{Per cent Cr}_2\text{O}_3}{0.253} \right) + \left(\frac{\text{Per cent Al}_2\text{O}_3}{0.170} \right) + \left(\frac{\text{Per cent Fe}_2\text{O}_3}{0.266} \right)$$

$$\text{Per cent acidity} = \text{acidity} \times 100$$

¹ Expressed as a decimal fraction.

CHROMIUM CHLORIDE

Chromium chloride is analyzed exactly like chromium sulfate, with a few differences in detail.

Insoluble Matter, Chromium, Iron, and Aluminum.—Determine exactly as directed under analysis of chromium sulfate.

Acid Chloride.—Determine as directed under determination of acid sulfate in chromium sulfate, but calculate and report percentage of acid chloride as chlorine.

$$\text{Per cent acid chloride as Cl} = \frac{\text{cc. 0.1-N NaOH required} \times 0.3546}{\text{g. sample weighed}}$$

Neutral Chloride as Sodium Chloride.—Weigh accurately about 0.5 g., and determine total chloride as directed under analysis of chromium sulfate. Calculate as percentage of chlorine. Subtract percentage of acid chloride, and calculate the difference as sodium chloride.

$$\text{Per cent NaCl} = (\text{per cent total Cl} - \text{per cent acid Cl}) \times 1.648$$

Sulfate.—Weigh accurately about 2 g., and determine as directed under determination of total sulfate in chromium sulfate. Calculate as percentage of sodium sulfate.

$$\text{Per cent} = \frac{\text{g. BaSO}_4 \times 60.87}{\text{g. sample weighed}}$$

Acidity of Chromium Salt.—Determine exactly as directed for chromium sulfate, using the number of cubic centimeters of tenth-normal sodium hydroxide required for the titration of 1 g. of the salt in the determination of acid chloride.

ONE-BATH CHROME LIQUORS (1, 3, 5, 6, 8, 13, 20, 21, 24 to 29, 31, 34 to 36, 38, 40 to 42, 44, 45)

One-bath chrome liquors, as freshly prepared, are dilute solutions of a chrome tanning compound, which is most often the basic sulfate but may be the chloride. To this solution are sometimes added sodium chloride, sodium sulfate, alum, and various other compounds. The complete analysis of such a liquor would be carried out like that of chromium sulfate, using samples of size proportioned to the dilution. The most important characteristics of such a liquor are its chromium content, acidity of the chromium salt, and pH value. When pickled skins are introduced into the liquor, the chromium content falls, the pH value falls, and the content in neutral chloride or sulfate rises. Upon partial neutralization of the liquor by means of sodium bicarbonate or other alkali, the pH value rises, the chromium content falls still lower, and the neutral salt content increases. As it is highly important that the addition of alkali

should not proceed to the extent that chromium hydroxide is precipitated, the "precipitation figure" of the liquor is determined, simply by titrating a portion of the liquor with a standard solution of the alkali used until precipitation does take place and calculating the quantity of the alkali that can be added to the liquor with safety. The chromium content of a used chrome liquor is important in showing whether sufficient chromium has been fixed by the skin and, together with the pH value, whether successive tanning lots are being tanned under identical conditions.

The A. L. C. A. has adopted official methods for the determination of chromium, acid, and basicity in one-bath chrome liquors. These methods are given below, together with the methods used by the authors for determining pH value and precipitation value.

Official Methods of the A. L. C. A. (1). 1. *Chromium*.—Dilute a measured quantity of the liquor to a definite volume containing from 0.0015 to 0.0025 g. of chromic oxide per milliliter. To 10 ml. of this dilution add 50 ml. of water and 2 g. of sodium peroxide. Boil gently for 30 min., add water if necessary to keep the volume from falling below 15 ml., cool, and dilute to 150 ml. Neutralize with strong hydrochloric acid, and add 5 ml. in excess. Cool again, and add 10 ml. of a 10-per cent solution of potassium iodide. After 1 min. titrate with tenth-normal sodium thiosulfate. When the iodine color has nearly disappeared, add a few milliliters of starch solution (1 g. per liter), and titrate to the disappearance of blue. One milliliter of tenth-normal sodium thiosulfate is equivalent to 0.002533 g. chromic oxide.

2. *Acid*.—To 50 ml. of the dilution specified under the determination of Chromium, in a 7-in. porcelain dish, add about 400 ml. of water and 1 ml. of a 5-per cent solution of phenolphthalein and bring to boiling. While boiling, titrate with half-normal sodium hydroxide until the pink color persists after 1 min. One milliliter of half-normal sodium hydroxide is equivalent to 0.02002 g. of sulfur trioxide; 0.02452 g. of sulfuric acid; 0.01773 g. of chlorine; or 0.01823 g. of hydrochloric acid.

3. *Basicity*.—Express basicity according to Schlörlemmer's system. By this system the basicity is that percentage of the total chromic oxide that is combined with hydroxyl. For example: For $\text{Cr}_2(\text{SO}_4)_3$, or a neutral salt, the basicity is 0 per cent; for $\text{Cr}(\text{OH})(\text{SO}_4)$, or a one-third basic salt, it is $33\frac{1}{3}$ per cent; for $\text{Cr}_2(\text{OH})_2(\text{Cl})_2$, or a one-half basic salt, it is 50 per cent; and for chromic hydroxide $\text{Cr}(\text{OH})_3$, the basicity is 100 per cent. Thus the greater the basicity the higher the basicity figure.

Determine chromium and acid in the usual manner and calculate the basicity from the formula:

$$\text{Percentage basicity} = \frac{100(A - B)}{A}$$

in which A represents the percentage of total chromic oxide in the sample and B the percentage of chromic oxide combined with acid. If desired, quantity values instead of percentages may be used for A and B , provided the same quantity of sample is used as a basis for each value.

From the acid determination B is calculated as percentage of chromic oxide combined with acid by the following formula:

$$B = \frac{\text{NaOH} \times \text{g. NaOH per ml.}}{\text{amount of sample}}$$

in which 0.63321 g. is the quantity of chromic oxide precipitated by 1 g. of sodium hydroxide.

pH Value.—Determine by the electrometric method described in Chap. VII. Chromic solutions sometimes exert a poisoning action on the electrodes, which can be minimized by the following precautions: Be sure that the electrode is thoroughly saturated with hydrogen before introducing it into the chrome liquor. Take the reading as soon as the voltage ceases to change rapidly; the pH value of any chromic sulfate or chloride solution changes slowly for days after equilibrium is disturbed in any way. Always make the measurement in duplicate with different hydrogen electrodes. As soon as the electrode is removed from the liquor, place it in dilute sulfuric acid; if this is not done, the electrode can seldom be used for more than one determination without cleaning and replatinizing.

Precipitation Value (31).—Filter a portion of the chrome liquor through a dry filter with the aid of kaolin. Pipette 10 cc. into a clean, dry 50-cc. beaker of clear glass. Titrate with twentieth-molar sodium bicarbonate, carbonate, borate, phosphate, or hydroxide, depending upon which material is used in neutralizing the liquor in the tanning process. Add the solution a few drops at a time, swirling the liquor constantly, until the precipitate that forms where the alkali enters the liquor disappears somewhat slowly. Then add the solution 1 drop at a time, pausing for 15 sec. after each addition, until a faint turbidity is produced. This can best be observed by placing the beaker on the face of a watch and noting when the numerals become blurred. Calculate and report precipitation value in pounds of the particular material employed that will just produce a turbidity when added to 1 gal. of the chrome liquor.

Precipitation value = cc. 0.05- M solution per 10 cc. \times 0.834 \times factor
Factors:

1 cc. 0.05- M NaHCO_3	= 0.00420
Na_2CO_3 (soda ash)	= 0.00530
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (sal soda)	= 0.01432
$\text{Na}_2\text{B}_4\text{O}_7$	= 0.01006
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	= 0.01908
NaOH	= 0.00400
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (disodium phosphate)	= 0.01791

SODIUM DICHROMATE (4, 13, 37, 40)

Sodium (or potassium) dichromate is used as such in the two-bath chrome-tanning process and forms the starting point for

the preparation of the chrometanning compounds used in the one-bath process. Chromium is determined as in the analysis of chromic compounds, except that it is unnecessary to oxidize the chromium to the hexavalent state. The determination of chromium as chromium trioxide, CrO_3 , together with an acidimetric titration, gives the data from which can be calculated the distribution of chromium between chromate, dichromate, and chromic acid. Any impurities present (iron, aluminum, sulfate, chloride, etc.) may be determined by the same methods applied to chromium sulfate.

Chromium as Chromium Trioxide.—Weigh accurately about 4 g., dissolve in water, transfer to a 1-l. volumetric flask, and make up to the mark. Pipette 25 cc. into a 250-cc. Erlenmeyer flask, dilute to about 100 cc., add 10 cc. of concentrated hydrochloric acid and 10 cc. of a 10-per cent solution of potassium iodide. Titrate with approximately tenth-normal sodium thiosulfate (recently standardized as described in Chap. XIII) until the brown color is nearly discharged, then add about 1 cc. of starch indicator, and add the reagent drop by drop until the blue color changes to a clear sea green. Take the end point as the first complete disappearance of the blue, and ignore any return of color, due to air oxidation. Calculate and report percentage of chromium trioxide.

$$\text{Per cent CrO}_3 = \frac{\text{cc. approx. } 0.1-N \text{ Na}_2\text{S}_2\text{O}_3 \times \text{factor} \times 0.333}{\text{g. sample in 25 cc. solution}}$$

Free Chromic Acid, Sodium Dichromate, and Sodium Chromate.—This determination is based upon the following facts: To reduce 1 g.-mol. of chromium trioxide to chromic oxide requires 3 equivalents of sodium thiosulfate or other reducing agent. To neutralize 1 mol. of chromium trioxide to form a chromate (which reacts just alkaline to phenolphthalein) requires two equivalents of sodium hydroxide. If the chromic acid is already half neutralized to form a dichromate, only one equivalent of alkali is required for completing the neutralization. Therefore if the volume of tenth-normal sodium hydroxide required to neutralize a given volume of chromate solution to phenolphthalein is more than two-thirds of the volume of tenth-normal sodium thiosulfate required to reduce the same volume of chromate solution, the solution contains chromic acid plus another acid; if the ratio is exactly 2:1, the solution contains chromic acid only; if the ratio is less than 2:3 but more than 1:3, the solution contains chromic acid and dichromate; if the ratio is exactly 1:3, the solution contains dichromate only; if the ratio

is less than 1:3, the solution contains dichromate and chromate; and if no acid is required, the solution contains only neutral chromate.

Pipette exactly 50 cc. of the solution prepared as described under the determination of chromium trioxide into an Erlenmeyer flask, dilute to about 300 cc., add 5 drops of phenolphthalein indicator, and titrate with tenth-normal sodium hydroxide. The color changes from orange red to yellow, and at the end point an orange-pink shade is produced. Call the volume required A .

Calculate the volume of *exactly* tenth-normal sodium thiosulfate solution required to reduce 50 cc. of the solution, from the data obtained in determining chromium trioxide. Call the volume required B .

1. If $A \geq \frac{2}{3}B$,

Per cent free CrO_3 = per cent CrO_3 determined by thiosulfate titration

$$\text{Per cent additional acid as } \text{H}_2\text{SO}_4 = \frac{(A - \frac{2}{3}B) \times 0.49}{\text{g. sample in 50 cc.}}$$

2. If $A < \frac{2}{3}B$ but $A > \frac{1}{3}B$

$$\text{Per cent } \text{CrO}_3 = \frac{(A - \frac{1}{3}B) \times 0.500}{\text{g. sample in 50 cc.}}$$

$$\text{Per cent } \text{Na}_2\text{Cr}_2\text{O}_7 = \frac{\frac{1}{3}B \times 2.62}{\text{g. sample in 50 cc.}}$$

3. If $A \leq B$,

$$\text{Per cent } \text{Na}_2\text{Cr}_2\text{O}_7 = \frac{(B - A) \times 1.62}{\text{g. sample in 50 cc.}}$$

$$\text{Per cent } \text{Na}_2\text{Cr}_2\text{O}_7 = \frac{A \times 2.62}{\text{g. sample in 50 cc.}}$$

ALUMINUM SULFATE

Aluminum sulfate, either as such or in the form of alum, $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, is used to some extent in tanning and to a much greater extent as a mordant in dyeing leather. The analysis of either form of aluminum sulfate is carried out almost exactly like that of chromium sulfate. The determination of chromium is, of course, omitted. If the material is to be used in connection with coloring, the presence of small amounts of iron may be very objectionable. If present in considerable amounts, iron may be detected by the sodium peroxide separation method; but if this method does not show an appreciable percentage to be present, the colorimetric thiocyanate test should be applied.

Samples of aluminum sulfate analyzed in the authors' laboratory during the past 10 years have averaged: aluminum (as

oxide), 18.14 per cent; iron (as ferric oxide), 0.15 per cent; acid sulfate (as sulfur trioxide), 37.56 per cent; neutral sulfate (as sodium sulfate), 3.95 per cent; chloride (as sodium chloride), 0.40 per cent; insoluble matter, 0.18 per cent; and acidity of the aluminum salt, 0.87.

Insoluble Matter.—Weigh accurately about 10 g., and dissolve in about 250 cc. of water, filter, and wash the paper free from sulfates. Receive the filtrate and washings in a 1-l. volumetric flask, make up to volume, and use the solution for later determinations. Ignite the filter and insoluble matter in a weighed platinum crucible, cool in a desiccator, and weigh. Calculate and report percentage of insoluble matter.

$$\text{Per cent insoluble matter} = \frac{\text{g. insoluble matter} \times 100}{\text{g. sample weighed}}$$

Analysis.—If the percentage of insoluble matter exceeds 0.5, determine silica, aluminum, iron, calcium, and magnesium as directed under analysis of ash of vegetable-tanned leather (Chap. II).

Iron.—Weigh accurately about 0.5 g. into a 400-cc. beaker, dissolve in about 200 cc. of water, make the solution strongly acid with hydrochloric acid, boil, and filter if necessary. To the filtrate add pure, solid sodium carbonate until a copious precipitate forms, then add about 1 g. of pure sodium peroxide (free from iron and aluminum), and boil until most of the precipitate redissolves. If iron is present in weighable amounts, a brownish residue will remain undissolved. Filter, and wash 5 or 6 times with hot water. Save filtrate and washings for the determination of aluminum. Redissolve the iron hydroxide in hydrochloric acid, and reprecipitate with ammonia. Ignite in a weighed porcelain crucible, cool in a desiccator, and weigh as ferric oxide. Report percentage of iron as ferric oxide.

$$\text{Per cent Fe}_2\text{O}_3 = \frac{\text{g. Fe}_2\text{O}_3 \times 100}{\text{g. sample weighed}}$$

In the absence of appreciable amounts of precipitate insoluble in sodium hydroxide solution, test for iron by the colorimetric method described under analysis of water (Chap. VIII).

Use the filtrate from iron for the determination of aluminum.

Aluminum.—To the filtrate from iron add hydrochloric acid until the solution is acid. Add a few drops of methyl red indicator, and add ammonium hydroxide, drop by drop, until the color changes to yellow. Boil the solution until the yellow color changes back to pink, filter at once, and wash three times with hot water. Dissolve the precipitate in dilute hydrochloric acid, receiving the solution in the beaker used for the first precipitation, wash the paper free from chlorides, and reprecipitate aluminum hydroxide as before. Filter and wash free from chlorides with hot water. Dry the paper and precipitate at about 105°C., ignite in a tared porcelain crucible at bright red heat, cool, and weigh. Calculate and report percentage of aluminum as oxide.

$$\text{Per cent Al}_2\text{O}_3 = \frac{\text{g. sample weighed}}{\text{g. sample weighed}}$$

Calcium, Magnesium.—If desired, determine calcium and magnesium in the filtrate from aluminum, as directed under analysis of ash of vegetable-tanned leather (Chap. II).

Acid Sulfate.—Determine as directed under analysis of chromium sulfate. Calculate and report percentage of acid sulfate as sulfur trioxide.

Neutral Sulfate.—Determine total sulfate, and calculate percentage of neutral sulfate as sodium sulfate, as directed under analysis of chromium sulfate.

Chloride.—Determine exactly as directed under analysis of chromium sulfate. Calculate and report as percentage of sodium chloride.

Acidity of Aluminum Salt.—Calculate as directed under analysis of chromium sulfate, using the modified equation

$$\text{Acidity} = \frac{\text{cc. 0.1-N NaOH consumed by 1 g.}}{\left(\frac{\text{Per cent Al}_2\text{O}_3}{0.170} \right) \times \left(\frac{\text{Per cent Fe}_2\text{O}_3}{0.266} \right)}$$

SULFURIC ACID (VITRIOL) (12, 27, 37, 40)

Sulfuric acid is used extensively in pickling skins prior to chrome tanning, also in bleaching vegetable-tanned leather and for numerous miscellaneous uses in the tannery.

Commercial vitriol contains 93 to 94 per cent sulfuric acid (sp. gr. 1.83 to 1.84) and should contain only traces of non-volatile matter. The strength of the acid may be determined from the specific gravity, provided this does not exceed 1.8354; otherwise by titration. Other determinations performed are those of non-volatile matter (and its analysis if the percentage found is appreciable) and chlorides. The completeness of the analysis depends in large measure upon the purpose for which the acid is to be used. For pickling skins, small amounts of impurities are not seriously objectionable.

Specific Gravity at 60°F.—Place about 500 cc. of acid in a glass-stoppered bottle, and immerse up to the neck in cold water until the temperature of the acid is a little below 60°F. Pour the acid into a dry hydrometer cylinder, put in a hydrometer with a scale range including 1.84, stir the acid with a thermometer until the temperature is exactly 60°F., and read the specific gravity.

The hydrometer employed may read directly in specific gravity units or in degrees Baumé. The relation between these two scales is given in Table 45.

Sulfuric Acid.—If the specific gravity found does not exceed 1.8354 (=66° Bé.), determine percentage of sulfuric acid from the specific gravity by consulting Table 45.

TABLE 45.—SPECIFIC GRAVITY AND PERCENTAGE OF SULFURIC ACID¹

Degrees Baumé	Specific gravity 60°F. 60°F.	Degrees Twaddell	Per cent sulfuric acid
0	1.0000	0.0	0.00
1	1.0069	1.4	1.02
2	1.0140	2.8	2.08
3	1.0211	4.2	3.13
4	1.0284	5.7	4.21
5	1.0357	7.1	5.28
6	1.0432	8.6	6.37
7	1.0507	10.1	7.45
8	1.0584	11.7	8.55
9	1.0662	13.2	9.66
10	1.0741	14.8	10.77
11	1.0821	16.4	11.89
12	1.0902	18.0	13.01
13	1.0985	19.7	14.13
14	1.1069	21.4	15.25
15	1.1154	23.1	16.38
16	1.1240	24.8	17.53
17	1.1328	26.6	18.71
18	1.1417	28.3	19.89
19	1.1508	30.2	21.07
20	1.1600	32.0	22.25
21	1.1694	33.9	23.43
22	1.1789	35.8	24.61
23	1.1885	37.7	25.81
24	1.1983	39.7	27.03
25	1.2083	41.7	28.28
26	1.2185	43.7	29.53
27	1.2288	45.8	30.79
28	1.2393	47.9	32.05
29	1.2500	50.0	33.33
30	1.2609	52.2	34.63
31	1.2719	54.4	35.93
32	1.2832	56.6	37.26
33	1.2946	58.9	38.58
34	1.3063	61.3	39.92
35	1.3182	63.6	41.27
36	1.3303	66.1	42.63
37	1.3426	68.5	43.99
38	1.3551	71.0	45.35
39	1.3679	73.6	46.72

¹ Data for 0 to 66° Baumé by W. C. Ferguson and H. P. Talbot; adopted as standard by the Manufacturing Chemists' Association of the United States, June 23, 1904. Data for 94 to 100-per cent sulfuric acid by H. B. Bishop.

TABLE 45.—SPECIFIC GRAVITY AND PERCENTAGE OF SULFURIC ACID.—
(Continued)

Degrees Baumé	Specific gravity 60°F. 60°F.	Degrees Twaddell	Per cent sulfuric acid
40	1.3810	76.2	48.10
41	1.3942	78.8	49.47
42	1.4078	81.6	50.87
43	1.4216	84.3	52.26
44	1.4356	87.1	53.66
45	1.4500	90.0	55.07
46	1.4646	92.9	56.48
47	1.4796	95.9	57.90
48	1.4948	99.0	59.32
49	1.5104	102.1	60.75
50	1.5263	105.3	62.18
51	1.5426	108.5	63.66
52	1.5591	111.8	65.13
53	1.5761	115.2	66.63
54	1.5934	118.7	68.13
55	1.6111	122.2	69.65
56	1.6292	125.8	71.17
57	1.6477	129.5	72.75
58	1.6667	133.3	74.36
59	1.6860	137.2	75.99
60	1.7059	141.2	77.67
61	1.7262	145.2	79.43
62	1.7470	149.4	81.30
63	1.7683	153.7	83.34
64	1.7901	158.0	85.66
64 $\frac{1}{4}$	1.7957	159.1	86.33
64 $\frac{1}{2}$	1.8012	160.2	87.04
64 $\frac{3}{4}$	1.8068	161.4	87.81
65	1.8125	162.5	88.65
65 $\frac{1}{4}$	1.8182	163.6	89.55
65 $\frac{1}{2}$	1.8239	164.8	90.60
65 $\frac{3}{4}$	1.8297	165.9	91.80
66	1.8354	167.1	93.19
	1.8381	94.00
	1.8407	95.00
	1.8427	96.00
	1.8437	97.00
	1.8439	97.50
	1.8437	98.00
	1.8424	99.00
	1.8391	100.00

If the specific gravity exceeds this value, determine sulfuric acid by titration. Weigh accurately a small glass-stoppered weighing bottle, previously dried at about 100°C. Introduce into the bottle about 3 cc. of acid from a small pipette, stopper, and reweigh. Place the stoppered bottle in a beaker containing about 200 cc. of distilled water, remove the stopper by means of a glass rod bent into a hook, stir, fish out the bottle and stopper, and rinse them with a wash-bottle stream. Transfer the solution to a 1-l. volumetric flask, and make up to the mark. Pipette 50 cc. of the solution into a titrating vessel, dilute to about 150 cc., add 2 drops of methyl red indicator, and titrate with tenth-normal sodium hydroxide until the solution turns yellow. Calculate and report percentage of total acid as sulfuric.

$$\text{Per cent H}_2\text{SO}_4 = \frac{\text{cc. 0.1-N NaOH} \times 0.49}{\text{g. sample in 50 cc. of solution}}$$

Non-volatile Matter.—Weigh rapidly to the nearest 0.1 g. about 10 g. of acid in a weighed platinum dish. Evaporate on a sand bath or asbestos gauze under a good hood until no more fumes of sulfur trioxide are evolved, then ignite at dull red heat over a free flame. Cool in a desiccator, and weigh. Calculate and report percentage of non-volatile matter.

$$\text{Per cent non-volatile matter} = \frac{\text{g. non-volatile matter} \times 100}{\text{g. sample weighed}}$$

Analysis.—If percentage of non-volatile matter exceeds 0.1, determine iron, aluminum, calcium, and magnesium as directed under analysis of ash of vegetable-tanned leathers (Chap. II). Calculate and report as percentages of the corresponding sulfates.

$$\begin{aligned}\text{FeSO}_4 &= \text{Fe}_2\text{O}_3 \times 1.9 \\ \text{Al}_2(\text{SO}_4)_3 &= \text{Al}_2\text{O}_3 \times 3.35 \\ \text{CaSO}_4 &= \text{CaO} \times 2.43 \\ \text{MgSO}_4 &= \text{MgO} \times 2.99\end{aligned}$$

Hydrochloric Acid.—Test a portion of the solution prepared for the determination of sulfuric acid by adding a few drops of silver nitrate solution. If no precipitate or only a faint turbidity is produced, chlorides may be considered absent. If an appreciable precipitate forms, weigh accurately about 10 g. of acid from a stoppered weighing bottle, and dissolve in about 200 cc. of water. Add a few drops of phenolphthalein indicator, and add 10-per cent sodium carbonate solution (free from chlorides) from a pipette until a faint pink color is produced, then make slightly acid with acetic acid. Add a few drops of potassium chromate indicator, and titrate with tenth-normal silver nitrate to the formation of a brick-red precipitate of silver chromate. Calculate and report percentage of chlorine as hydrochloric acid.

$$\text{Per cent HCl} = \frac{0.1\text{-N AgNO}_3}{\text{g. sample weighed}}$$

HYDROCHLORIC ACID (MURIATIC ACID)(12, 37, 40)

The grade of hydrochloric acid generally employed in the tannery is muriatic acid (sp. gr. 1.12) containing about 24 per cent hydrochloric acid. The principal impurity is iron chloride. The analysis consists of the determination of hydrochloric acid by titration or from the specific gravity, non-volatile matter, and iron chloride.

Specific Gravity.—Determine as directed under analysis of sulfuric acid, using a hydrometer of suitable range.

Hydrochloric Acid.—Determine percentage of hydrochloric acid from the specific gravity by consulting Table 46, or by titration, using the procedure give under determination of sulfuric acid, using a sample of about 15 g. per 1. Calculate and report percentage of total acid as hydrochloric acid.

$$\text{Per cent HCl} = \frac{\text{cc. 0.1-N}}{\text{g. sample in 50 cc. of solution}} \times 0.3646$$

TABLE 46.—SPECIFIC GRAVITY AND PERCENTAGE OF ACID¹

Degrees Baumé	Specific gravity 60°F. 60°F.	Degrees Twaddell	Per cent hydrochloric acid
1.00	1.0069	1.38	1.40
2.00	1.0140	2.80	2.82
3.00	1.0211	4.22	4.25
4.00	1.0284	5.68	5.69
5.00	1.0357	7.14	7.15
5.25	1.0375	7.50	7.52
5.50	1.0394	7.88	7.89
5.75	1.0413	8.26	8.26
6.00	1.0432	8.64	8.64
6.25	1.0450	9.00	9.02
6.50	1.0469	9.38	9.40
6.75	1.0488	9.76	9.78
7.00	1.0507	10.14	10.17
7.25	1.0526	10.52	10.55
7.50	1.0545	10.90	10.94
7.75	1.0564	11.28	11.32
8.00	1.0584	11.68	11.71
8.25	1.0603	12.06	12.09
8.50	1.0623	12.46	12.48
8.75	1.0642	12.84	12.87
9.00	1.0662	13.24	13.26
9.25	1.0681	13.62	13.65
9.50	1.0701	14.02	14.04
9.75	1.0721	14.42	14.43

TABLE 46.—SPECIFIC GRAVITY AND PERCENTAGE OF HYDROCHLORIC ACID.¹—(Continued)

Degrees Baumé	Specific gravity 60°F. 60°F.	Degrees Twaddell	Per cent hydrochloric acid
10.00	1.0741	14.82	14.83
10.25	1.0761	15.22	15.22
10.50	1.0781	15.62	15.62
10.75	1.0801	16.02	16.01
11.00	1.0821	16.42	16.42
11.25	1.0841	16.82	16.81
11.50	1.0861	17.22	17.21
11.75	1.0881	17.62	17.61
12.00	1.0902	18.04	18.01
12.25	1.0922	18.44	18.41
12.50	1.0943	18.86	18.82
12.75	1.0964	19.28	19.22
13.00	1.0985	19.70	19.63
13.25	1.1006	20.12	20.04
13.50	1.1027	20.54	20.45
13.75	1.1048	20.96	20.86
14.00	1.1069	21.38	21.27
14.25	1.1090	21.80	21.68
14.50	1.1111	22.22	22.09
14.75	1.1132	22.64	22.50
15.00	1.1154	23.08	22.92
15.25	1.1176	23.52	23.33
15.50	1.1197	23.94	23.75
15.75	1.1219	24.38	24.16
16.00	1.1240	24.80	24.57
16.2	1.1256	25.12	24.90
16.4	1.1274	25.48	25.23
16.6	1.1292	25.84	25.56
16.8	1.1310	26.20	25.89
17.0	1.1328	26.56	26.22
17.2	1.1345	26.90	26.56
17.4	1.1363	27.26	26.90
17.6	1.1381	27.62	27.24
17.8	1.1399	27.98	27.58
18.0	1.1417	28.34	27.92
18.2	1.1435	28.70	28.26
18.4	1.1453	29.06	28.61
18.6	1.1471	29.42	28.95
18.8	1.1489	29.78	29.30
19.0	1.1508	30.16	29.65

TABLE 46.—SPECIFIC GRAVITY AND PERCENTAGE OF HYDROCHLORIC ACID.¹—(Continued)

Degrees Baumé	Specific gravity 60°F. 60°F.	Degrees Twaddell	Per cent hydrochloric acid
19.2	1.1526	30.52	30.00
19.4	1.1544	30.88	30.35
19.6	1.1563	31.26	30.71
19.8	1.1581	31.62	31.08
20.0	1.1600	32.00	31.45
20.2	1.1619	32.38	31.82
20.4	1.1637	32.74	32.19
20.6	1.1656	33.12	32.56
20.8	1.1675	33.50	32.93
21.0	1.1694	33.88	33.31
21.2	1.1713	34.26	33.69
21.4	1.1732	34.64	34.07
21.6	1.1751	35.02	34.45
21.8	1.1770	35.40	34.83
22.0	1.1789	35.78	35.21
22.2	1.1808	36.16	35.59
22.4	1.1827	36.54	35.97
22.6	1.1846	36.92	36.35
22.8	1.1866	37.32	36.73
23.0	1.1885	37.70	37.14
23.2	1.1904	38.08	37.58
23.4	1.1924	38.48	38.03
23.6	1.1944	38.88	38.49
23.8	1.1963	39.26	38.95
24.0	1.1983	39.66	39.41
24.2	1.2003	40.06	39.86
24.4	1.2023	40.46	40.32
24.6	1.2043	40.86	40.78
24.8	1.2063	41.26	41.24
25.0	1.2083	41.66	41.72
25.2	1.2103	42.06	42.30
25.4	1.2124	42.48	43.01

¹ Data by W. C. Ferguson; adopted as standard by the Manufacturing Chemists' Association of the United States, May 14, 1903.

Non-volatile Matter.—Determine as directed under analysis of sulfuric acid.

Iron Chloride.—Pipette 10 cc. of acid into a beaker, dilute to about 200 cc., add a few drops of methyl red indicator, and add ammonia slowly until the color changes. Boil for 1 min., filter at once, and wash free from chlorides with hot water. Dry the paper and precipitate at about

100°C., ignite in a weighed crucible, cool in a desiccator, and weigh as iron oxide. Calculate and report percentage of ferric chloride.

$$\text{Per cent FeCl}_3 = \frac{\text{g. Fe}_2\text{O}_3 \times 203.2}{10 \times \text{sp. gr. of acid}}$$

PICKLE LIQUORS

Pickle liquors contain an acid, generally sulfuric, in quantity sufficient to bring the skins to a slightly acid state and salt in quantity sufficient to repress swelling of the skin by the acid. Pickling brings the skins to the proper acidity for tanning with chrome salts, removes iron stains, converts any lime present to calcium sulfate, and brings the skins to a state in which they can be preserved without damage for a long time. Many skins, particularly sheepskins, are pickled after unhairing merely for purposes of preservation, being subsequently depickled with sodium carbonate before tanning.

The scheme of control of pickling by means of chemical analysis varies with the scheme of pickling employed. In any scheme of pickling it is highly important that the salt concentration of the liquor should be sufficiently high to prevent swelling, with a liberal margin of safety. A concentration of 1 lb. per gallon (about 12 per cent) accomplishes this end. If the skins are pickled in a drum with a comparatively small volume of liquor, it must be remembered that the initial concentration will be materially reduced by the liquor introduced in the skins—from 60 to 80 per cent of their wet weight—and the initial salt content increased accordingly. Salt concentration is best determined by means of a hydrometer, as the amount of acid present is too small to affect the specific gravity appreciably. The quantity of acid in the liquor should be sufficient to neutralize the lime in the skins and to combine with all or most of the protein. In order to guarantee that enough will be present, an excess is generally employed. The determination of acid in the used liquors tells whether a sufficient excess was employed and makes it possible to calculate the quantity of acid neutralized and absorbed per pound of skin. Variations in this quantity from lot to lot or from day to day indicate variable removal of lime from the skins in the beamhouse, from which irregularities in operating can often be detected. In paddle pickling, the liquor is often used over and over, salt being added each time to maintain a fixed concentration and acid added in proportion to the weight of each pack pickled.

Vitriol.—Titrate 100 cc. of pickle liquor with standard sodium hydroxide, using phenolphthalein indicator. If the vitriol used is measured in fluid ounces, the strength of the sodium hydroxide should be such that the results can be reported in terms of fluid ounces of vitriol per 100 gal. with a minimum of calculation. If the alkali is exactly 0.2785-normal, each cubic centimeter consumed by 100 cc. of pickle liquor is equivalent to 1 fl. oz. of vitriol (sp. gr. 1.84) in 100 gal.

Salt.—Determine the specific gravity of the liquor with a hydrometer. An instrument known as the "saltometer" is especially designed for this measurement. This instrument reads in degrees; 100° is equivalent to complete saturation at 15°C., or 317.9 g. of sodium chloride per liter. Each degree therefore means 3.18 g. of salt per liter, or 0.0265 lb. per gallon.

Table 47, calculated from Gerlach's data, shows the relation between specific gravity at 15°C., percentage of salt by weight, grams per liter, pounds per gallon, and saltometer reading.

TABLE 47.—SPECIFIC GRAVITY OF SODIUM CHLORIDE SOLUTIONS AT 15°C.

Specific gravity	Per cent sodium chloride by weight	Grams sodium chloride per liter	Pounds sodium chloride per gallon	Saltometer degrees
1.0000	0	0.0	0.00	0
1.0072	1	10.1	0.08	3
1.0145	2	20.3	0.17	7
1.0217	3	30.7	0.26	10
1.0290	4	41.1	0.34	14
1.0362	5	51.8	0.43	17
1.0437	6	62.6	0.52	21
1.0511	7	73.6	0.61	24
1.0585	8	84.7	0.71	28
1.0659	9	95.9	0.80	32
1.0733	10	107.3	0.89	36
1.0810	11	118.9	0.99	39
1.0886	12	130.6	1.09	43
1.0962	13	142.5	1.19	47
1.1038	14	154.5	1.29	51
1.1115	15	166.7	1.39	55
1.1194	16	179.1	1.49	59
1.1273	17	191.6	1.60	63
1.1352	18	204.3	1.70	66
1.1431	19	217.2	1.81	70
1.1511	20	230.2	1.92	74
1.1593	21	243.5	2.03	78
1.1675	22	256.8	2.14	82
1.1758	23	270.4	2.25	86
1.1840	24	284.1	2.37	91
1.1923	25	298.1	2.49	95
1.2010	26	312.3	2.60	99
1.2034	26.395	317.9	2.65	100

SODIUM THIOSULFATE ("HYPO") (12, 37)

Sodium thiosulfate is used to reduce bichromate to a chromic salt in the two-bath chrome-tanning process. The most important determination in its analysis is that of sodium thiosulfate, made by measuring its reducing power iodimetrically. Qualitative, and if necessary quantitative, tests are made for insoluble matter, iron and alumina, calcium, magnesium, sulfates, and chlorides. Sodium thiosulfate dissolves to form a solution that is practically neutral to phenolphthalein; should an alkaline solution be produced, the material should be examined for carbonates and sulfates; if acid, for bisulfites.

Weigh exactly 20 g. of the material, dissolve in water in a 500-cc. volumetric flask, and make up to the mark. Place in a 500-cc. Erlenmeyer flask about 10 cc. of 10-per cent potassium iodide solution and 10 cc. of strong hydrochloric acid, and add from a pipette exactly 100 cc. of exactly tenth-normal potassium dichromate solution. Let the solution stand for a few minutes, then add the thiosulfate solution from a burette until the brown color is almost discharged. Add a few drops of starch indicator, and continue to add thiosulfate drop by drop until the blue color changes to a clear sea green. Take the first complete disappearance of blue as the end point, and ignore any return of color, which is due to air oxidation.

Calculate and report total reducing power as sodium thiosulfate.

$$\text{Per cent Na}_2\text{S}_2\text{O}_3 = \frac{\text{cc. thiosulfate solution required}}{\text{cc. thiosulfate solution required}}$$

$$\text{Per cent Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = \frac{\text{cc. thiosulfate solution required}}{\text{cc. thiosulfate solution required}}$$

Sulfites, Bisulfites, Carbonates, and Bicarbonates.—Pure sodium thiosulfate is practically neutral, and its solution requires only a few drops of alkali or acid to change the color of either phenolphthalein or methyl orange indicator. Test 50 cc. of the sodium thiosulfate solution prepared as described above with phenolphthalein and with methyl orange, and determine the volume of tenth-normal sodium hydroxide or of tenth-normal sulfuric acid required to neutralize the solution to each of these indicators. If more than a few drops are consumed in any one of these titrations, the material contains either sodium carbonate or sulfite (if alkaline to phenolphthalein) or sodium bicarbonate or bisulfite (if alkaline to methyl orange and acid to phenolphthalein). In either of these cases, sulfites and carbonates may be determined as described under analysis of sodium sulfite.

Insoluble Matter, Iron and Aluminum, Calcium, and Magnesium.—Determine as directed under analysis of sodium chloride (Chap. VIII).

Chlorides.—Pipette 50 cc. of the thiosulfate solution, prepared as described above, acidify with nitric acid, and add a few drops of tenth-normal silver nitrate solution. If more than a faint turbidity is produced, determine

chlorine by the Volhard method as described under analysis of lime liquors (Chap. VIII). Calculate as percentage of sodium chloride.

$$\text{Per cent NaCl} = \frac{\text{cc. 0.1-N } \text{---}}{\text{g. sample in } \text{---}} \quad \frac{0.5846}{\text{--- solution}}$$

Sulfates.—Pipette 50 cc. of the thiosulfate solution into a beaker, acidity with hydrochloric acid, and boil 5 min. to expel sulfur dioxide from any sulfites that may be present. Then precipitate and weigh sulfate as barium sulfate in the usual way. Calculate as percentage of sodium sulfate.

$$\text{Per cent Na}_2\text{SO}_4 = \frac{\text{g. BaSO}_4 \times 60.86}{\text{g. sample in 50 cc. solution}}$$

SULFITES (7, 9, 12, 18, 37, 43)

Sulfites, in the form of sulfur dioxide, sulfurous acid, sodium bisulfite, or sodium sulfite, are used to reduce bichromate to chromic salts in preparing 1-bath chrome tanning compounds and also to some extent in bleaching leather. Sulfurous acid is generally sold in the form of liquid SO_2 compressed in cylinders and is used by running it into the solution to be reduced. The bisulfite comes both as a solid, which is really the metabisulfite, $\text{Na}_2\text{S}_2\text{O}_5$, or as a strong solution. The sulfite is encountered less frequently, since it is less rich in the active constituent, sulfur dioxide.

The sulfur dioxide content of any of these sulfites is determined iodimetrically. The distribution of the sulfur dioxide between sulfurous acid, sodium bisulfite, and sodium sulfite is determined by titration and depends upon the fact that sulfurous acid is acid to methyl orange, sodium bisulfite is neutral to methyl orange but acid to phenolphthalein and sodium sulfite is neutral to phenolphthalein.

Tests for chlorides, sulfates, and metals other than sodium are performed in the usual way.

Samples of solid sodium bisulfite analyzed in the authors' laboratory have contained about 99 per cent of sodium bisulfite, NaHSO_3 , or 61 per cent of sulfur dioxide. Samples of liquid bisulfite have contained from 31 to 41 per cent of sodium bisulfite or 19 to 25 per cent of sulfur dioxide.

Total Sulfur Dioxide.—Weigh exactly 5.0000 g. of the solid or 10.0000 g. of the liquid sulfite, dissolve in water in a 500-cc. volumetric flask, and make up to the mark. Place in a 500-cc. Erlenmeyer flask about 10 cc. of 10-per cent potassium iodide solution and 10 cc. of strong hydrochloric acid. Add from a pipette exactly 100 cc. of tenth-normal potassium dichromate. Let the solution stand in the dark for 5 min. Titrate the

liberated iodine with the sulfite solution, added from a burette, as described under analysis of sodium thiosulfate.

Calculate and report percentage of total sulfur dioxide.

$$\text{Per cent SO}_2 = \frac{16,015}{\text{cc. sulfite solution required} \times \text{g. sample in 500 cc.}}$$

NOTE.—The sulfite must be added to the bichromate, not *vice versa*.

Sulfurous Acid, Bisulfite, Sulfite, and Free Alkali.—Test portions of the solution prepared as described above with methyl orange and phenolphthalein indicators. If the solution is acid to methyl orange, it contains sulfurous acid and sodium bisulfite (Case 1). If alkaline to methyl orange but acid to phenolphthalein, it contains sodium bisulfite and sodium sulfite (Case 2). If alkaline to phenolphthalein, it contains sodium sulfite and free alkali (sodium hydroxide or sodium carbonate) (Case 3).

Case 1.—Pipette exactly 50 cc. of the solution into an Erlenmeyer flask, dilute to about 150 cc., add a few drops of methyl orange indicator, and titrate with tenth-normal sodium hydroxide until the solution changes to a color intermediate between red and yellow, using comparison solutions made just acid and just alkaline to methyl orange, respectively. Call the volume required *A*. Repeat the titration with a fresh 50-cc. portion of solution and phenolphthalein indicator. Call the volume of alkali consumed *B*. Calculate and report percentage of sulfurous acid and of sodium bisulfite.

$$\text{Per cent H}_2\text{SO}_3 = \frac{A \times 0.82}{\text{g. sample in 50 cc.}}$$

$$\text{Per cent NaHSO}_3 = \frac{(B - A) \times 1.04}{\text{g. sample in 50 cc.}}$$

Case 2.—Pipette exactly 50 cc. of the sulfite solution into an Erlenmeyer flask, dilute to about 150 cc., add a few drops phenolphthalein indicator, and titrate with tenth-normal sodium hydroxide till the solution turns faintly pink. Call the volume of alkali required *A*. Then add methyl orange indicator, and titrate to the neutral point with tenth-normal sulfuric acid. Call the volume of acid required *B*. Calculate and report percentage of sodium bisulfite and of sodium sulfite.

$$\text{Per cent NaHSO}_3 = \frac{A \times 1.04}{\text{g. sample in 50 cc.}}$$

$$\text{Per cent Na}_2\text{SO}_3 = \frac{(B - A) \times 1.26}{\text{g. sample in 50 cc.}}$$

Case 3.—Pipette exactly 50 cc. of the sulfite solution into an Erlenmeyer flask, and titrate with tenth-normal sodium hydroxide until the solution is neutral to phenolphthalein. Call the volume of alkali consumed *A*. Then add methyl orange, and continue the titration with tenth-normal sodium hydroxide until the solution is again neutralized. Call the additional volume required *B*. Calculate and report free alkali as percentage of sodium hydroxide and of sodium sulfite.

$$\text{Per cent NaOH} = \frac{A \times 0.40}{\text{g. sample in 50 cc.}}$$

$$\text{Per cent Na}_2\text{SO}_3 = \frac{B \times 1.26}{\text{g. sample in 50 cc.}}$$

NOTE.—If the percentage of total sulfur dioxide found iodimetrically exceeds that calculated from the percentages of sulfurous acid, sodium bisulfite, and sodium sulfite found acidimetrically, the sample contains some other reducing substance, probably sodium thiosulfite. If the percentage of total sulfur dioxide found iodimetrically is less than that calculated from the acidimetric determinations, the sample contains some other acid or base, probably sulfuric acid if the sample is acid or sodium carbonate if the sample is alkaline.

Carbonate.—Determine carbon dioxide by the evolution method described under analysis of lime (Chap. VIII), with the following modifications (37): Use concentrated sulfuric acid to liberate the carbon dioxide, place several grams of solid potassium dichromate in the evolution flask to oxidize the liberated sulfur dioxide, and include in the train a wash bottle containing strong sulfuric acid and chromic acid to oxidize any sulfur dioxide escaping from the flask. Calculate and report percentage of sodium carbonate.

$$\text{Per cent Na}_2\text{CO}_3 = \frac{\text{g. CO}_2 \times 241}{\text{g. sample weighed}}$$

Insoluble Matter, Iron and Aluminum, Calcium, and Magnesium.—Determine as directed under analysis of sodium thiosulfate.

Sulfates, Chlorides.—Determine as directed under analysis of sodium thiosulfate.

SODIUM CARBONATE AND BICARBONATE (2, 12, 19, 30, 37)

These substances are analyzed by the same methods. As a rule, sodium bicarbonate contains a little carbonate, and *vice versa*. The carbonate is sold either as sal soda (the decahydrate) or as soda ash (anhydrous).

The average composition of samples of soda ash, sal soda, and sodium bicarbonate analyzed in the authors' laboratory is given in Table 48.

Water: In Soda Ash.—Weigh accurately about 5 g. into a weighed platinum dish. Dry at 105°C. overnight, desiccate, cool, and weigh. Calculate and report percentage of water.

In Sal Soda.—This compound melts in its own water of crystallization at 34°C., giving a solution that may spatter if evaporated at 105°C. Weigh accurately about 10 g. into a weighed platinum dish, place on a water bath until evaporated to dryness, then dry in the oven at 105°C. to constant weight. Calculate and report percentage of water.

$$\text{Per cent H}_2\text{O} = \frac{\text{Per cent loss in weight} \times 100}{\text{Per cent loss in weight}}$$

TABLE 48.—COMPOSITION OF SODA ASH, SAL SODA, AND SODIUM BICARBONATE

Constituent	Soda ash	Sal soda	Sodium bicarbonate
Water.....	0.10	0.26
Sodium carbonate..	94.80	37.98	2.80
Sodium bicarbonate	5.10	0.00	96.54
Insoluble matter....	Trace	0.00	0.00
Iron and alumina...	None	None	None
Sodium chloride....	Trace	None	0.36
Sodium sulfate.....	None	None	Trace

In Sodium Bicarbonate.—This substance gives up part of its “half-bound” carbonic acid at 105°C. Weigh accurately about 5 g. into a weighed platinum dish, and dry at 180 to 200°C. for 16 hr. Calculate percentage of loss in weight. Deduct percentage of half-bound carbonic acid calculated from the sodium bicarbonate found as described below, and report the difference as percentage of water.

$$\text{Per cent loss in weight} = \frac{\text{g. loss at } 200^{\circ}\text{C.} \times 100}{\text{g. sample}}$$

Per cent H_2O = per cent loss at 200°C. — (per cent $\text{NaHCO}_3 \times 0.375$)

Sodium Hydroxide, Carbonate, and Bicarbonate.—Weigh accurately about 10 g., and dissolve in 1 l. of water in a volumetric flask. Pipette exactly 25 cc. of this solution into an Erlenmeyer flask, dilute to about 100 cc. with recently boiled distilled water, add a few drops of phenolphthalein, and titrate with tenth-normal sulfuric acid until the pink color is just discharged. Call the volume required *A*. Add a few drops of methyl orange indicator, and continue to add tenth-normal sulfuric acid until the color of the solution changes to a color intermediate between yellow and orange red; using comparison solutions containing the same concentration of indicator, made just acid and just alkaline, respectively, to determine the end point. Call the additional volume of tenth-normal sulfuric acid *B*. If *A* exceeds *B*, the material contains sodium hydroxide and carbonate.

$$\text{Per cent NaOH} = \frac{(A - B) \times 0.40}{\text{g. sample in 25 cc.}}$$

$$\text{Per cent Na}_2\text{CO}_3 = \frac{2B \times 0.53}{\text{g. sample in 25 cc.}}$$

If *A* = *B*, the material contains sodium carbonate only.

$$\text{Per cent Na}_2\text{CO}_3 = \frac{(A + B) \times 0.53}{\text{g. sample in 25 cc.}}$$

If *B* exceeds *A*, the material contains sodium carbonate and bicarbonate.

$$\text{Per cent Na}_2\text{CO}_3 = \frac{2A \times 0.53}{\text{g. sample in 25 cc.}}$$

$$\text{Per cent NaHCO}_3 = \frac{(B - A) \times 0.84}{\text{g. sample in 25 cc.}}$$

Hydroxide and Carbonate: Carbonate Precipitation Method.—Pipette 25 cc. of the solution of the carbonate prepared as described above into an Erlenmeyer flask, add methyl orange indicator, and titrate with tenth-normal sulfuric acid to the neutral point. Call the volume of acid required *A*. Pipette 25 cc. of the solution into a 100-cc. volumetric flask, and add 10-per cent barium chloride solution, drop by drop, until precipitation of carbonate is complete, avoiding adding a large excess. Make up to the mark with recently boiled distilled water, and let stand until the precipitate has settled. Pipette 50 cc. of the clear solution into a flask, and titrate with tenth-normal sulfuric acid, using phenolphthalein indicator. Call the volume required *B*. Calculate and report percentage of sodium hydroxide and sodium carbonate.

$$\text{Per cent NaOH} = \frac{2B \times 0.40}{\text{g. sample in 25 cc. solution}}$$

$$\text{Per cent Na}_2\text{CO}_3 = \frac{(A - 2B) \times 0.53}{\text{g. sample in 25 cc.}}$$

Insoluble Matter.—Weigh accurately about 10 g., dissolve in about 200 cc. of water, and note whether any insoluble matter is present. If more than traces remain undissolved, filter the solution through ashless paper, wash with hot water until the washings are no longer alkaline to methyl red, ignite the paper in a weighed platinum crucible (porcelain is all right if the residue is not to be analyzed), cool in a desiccator, and weigh. Calculate percentage of insoluble matter.

$$\text{Per cent insoluble matter} = \frac{\text{g. insoluble matter} \times 100}{\text{g. sample}}$$

Iron, Aluminum, Calcium, and Magnesium.—These substances, if present in quantity, will be found in the insoluble matter. If the percentage of insoluble matter exceeds 0.5, fuse the insoluble matter with a little anhydrous sodium carbonate, dissolve the fusion in dilute hydrochloric acid, and determine iron, aluminum, calcium, and magnesium in the solution as described under analysis of sodium chloride (Chap. VIII). If little or no insoluble matter is present, iron may be determined by the colorimetric method described under analysis of water (Chap. VIII), in case the material is to be used for a process in which the presence of traces of iron is objectionable.

Sulfate.—Pipette 100 cc. of the solution prepared for the determination of hydroxide, carbonate, and bicarbonate into a 400-cc. beaker, acidify with hydrochloric acid, and boil. Determine sulfate by precipitation as barium sulfate, as described under analysis of sodium chloride (Chap. VIII). Calculate and report percentage of sulfate as sodium sulfate.

$$\text{Per cent Na}_2\text{SO}_4 = \frac{\text{g. BaSO}_4 \times 60.86}{\text{g. sample in 100 cc.}}$$

Chloride.—Pipette 100 cc. of the solution prepared as described above into a beaker, and make slightly acid with acetic acid. Add a few drops of

potassium chromate indicator, and titrate with tenth-normal silver nitrate, added drop by drop, till a permanent brick-red precipitate of silver chromate is formed. Calculate and report percentage of chloride as sodium chloride.

$$\text{Per cent NaCl} = \frac{\text{cc. } 0.1-N \text{ AgNO}_3 \times 0.5846}{\text{g. sample in 100 cc.}}$$

SODIUM BORATE (BORAX) (2, 12, 37)

Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is used as a mild alkali in a number of tannery operations, including the neutralization of chrome leather during or after tanning, fat liquoring, and stripping of vegetable-tanned leather. The analysis consists of the determination of sodium borate and the usual tests for impurities.

Samples of borax analyzed in the authors' laboratory have averaged about 54 per cent anhydrous borax, or about 99.5 per cent of the hydrate, 0.5 per cent sodium chloride, and traces of sodium sulfate and insoluble matter.

Weigh accurately about 10 g., dissolve in water in a 1-l. volumetric flask and make up to the mark. Pipette exactly 100 cc. into an Erlenmeyer flask, add a few drops of methyl orange indicator, heat to boiling, and titrate with half-normal sulfuric acid until the solution is exactly neutral, using acid and alkaline comparison solutions, if desired, to determine the end point. Record the volume of acid consumed. Pipette another 100-cc. portion of the solution into a second flask, heat to boiling, and add exactly the same volume of acid as before, omitting the indicator. Add 50 cc. of neutral glycerol, or 1 g. of mannitol, and 2 drops of phenolphthalein indicator. Titrate with half-normal sodium hydroxide until the solution turns a faint pink. Add 10 cc. more of glycerol, and continue the titration if the color is discharged. Repeat until the pink color does not disappear upon adding glycerol. Calculate and report percentage of sodium borate as the anhydride, $\text{Na}_2\text{B}_4\text{O}_7$, and percentage of the hydrate,

$$\text{Per cent Na}_2\text{B}_4\text{O}_7 = \frac{\text{cc. } 0.1-N \text{ NaOH} \times 2.52}{\text{g. sample in 100 cc.}}$$

$$\text{Per cent } \quad \quad \quad \text{per cent Na}_2\text{B}_4\text{O}_7 \times 1.894$$

Insoluble Matter, Iron, Aluminum, Sulfate, Chloride, Calcium, and Magnesium.—Determine as directed under analysis of sodium carbonate.

Free Alkali.—If the volume of half-normal sulfuric acid consumed in neutralizing the borax solution to methyl orange exceeds the volume of half-normal sodium hydroxide subsequently consumed in titrating with phenolphthalein in the presence of glycerol, calculate the difference as percentage of sodium hydroxide.

$$\text{Per cent NaOH} = \frac{\quad}{\text{g. sample in 100 cc.}} \times 2$$

SODIUM PHOSPHATE (12, 37)

Three sodium phosphates are known—trisodium phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, disodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, and monosodium phosphate, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. Trisodium phosphate gives strongly alkaline solutions, of pH value about 12; disodium phosphate gives slightly alkaline solutions, of pH value about 8; and monosodium phosphate gives slightly acid solutions, of pH value about 4. Trisodium and disodium phosphates are used for purposes similar to those served by sodium carbonate and bicarbonate, being good buffers and mild alkalies. Disodium phosphate has been used as a substitute for ammonium chloride in bating.

The analysis of any one of these phosphates consists of the determination of total phosphate and of the distribution of the phosphate between the several possible forms that may be present. The usual tests are performed for chlorides, sulfates, metals other than alkalies, and other impurities.

Total Phosphate.—Weigh accurately about 10 g., and dissolve in exactly 1 l. Pipette exactly 50 cc. of the solution into a beaker. If the solution is alkaline to phenolphthalein, add dilute hydrochloric acid, drop by drop, until the solution is just acid. Filter, if any insoluble matter is present, and wash thoroughly with cold water. To the filtrate add, drop by drop, with constant stirring, about 25 cc. of magnesia mixture (see below). Let the solution stand for 10 min., then add 25 cc. of strong ammonia solution per 100 cc. of solution. Allow the precipitate to settle overnight. Filter through a weighed Gooch crucible, wash about 6 times with a 1:4 solution of ammonia and twice with 10-per cent ammonium nitrate made alkaline with ammonia. Ignite the crucible gently over a Meker burner, gradually increasing the heat to the maximum temperature obtainable, until the residue is white or, at worst, a very light gray. Desiccate, cool, and weigh as magnesium pyrophosphate. Calculate and report as percentage of disodium or trisodium phosphate, depending upon which substance is being analyzed.

$$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} = \frac{\text{g. Mg}_2\text{P}_2\text{O}_7 \times 321.64}{\text{g. sample in 50 cc. soluti}}$$

Preparation of Magnesia Mixture.—Weigh roughly 110 g. of magnesium chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and dissolve in a small amount of water. Add about 280 g. of ammonium chloride and 700 cc. of ammonia, and dilute to 2 l. Allow the solution to stand for several hours, then filter, and preserve in a glass-stoppered bottle. A sediment, consisting of silica, which forms after long standing, can be filtered off.

Di- and Trisodium Phosphates by Titration.—Weigh accurately about 1 g. of trisodium phosphate, or 2 g. of disodium phosphate, and dissolve in about 50 cc. of water in a 250-cc. beaker. Determine the pH value of the solution with the hydrogen electrode, as described in Chap. VII. Titrate the solution with tenth-normal hydrochloric acid, determining the pH value of the solution after each addition, until the pH value has fallen below 4. If the material is the trisodium salt, the initial pH value will be about 12. Add tenth-normal hydrochloric acid, 2 cc. at a time, until the pH value has fallen to about 10.5; then add 0.2 cc. at a time until the pH value has fallen to about 7; then 2 cc. at a time until the pH value falls to about 6.5; then 0.2 cc. at a time until the pH value has fallen to about 3.5.

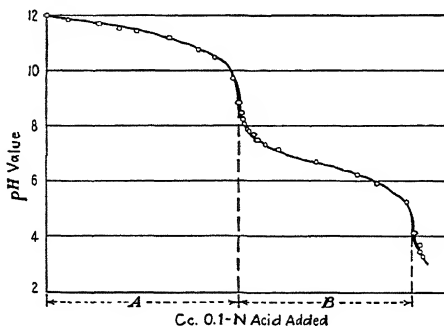


FIG. 73.—Titration of trisodium phosphate with tenth-normal acid. The volume *A* is that required to transform trisodium phosphate to disodium phosphate. The additional volume *B* is that required to change disodium phosphate to monosodium phosphate. If the original substance analyzed is disodium phosphate, the portion of the curve to the left of the first point of inflection will be missing.

Plot the volumes of acid added as abscissae and the corresponding pH values as ordinates, as shown in Fig. 73. The curve for trisodium phosphate has 2 points of inflection at which it passes through the vertical, one located near pH = 9, corresponding to the conversion of tri- to disodium phosphate, and the other located near pH = 4, corresponding to the conversion of di- to monosodium phosphate. In the case of a pure disodium phosphate, the portion of the curve for pH values above the first point of inflection will be missing. By dropping perpendiculars from the curve to the *x* axis at the points of inflection, as shown in Fig. 73, determine the volume of tenth-normal hydrochloric acid required to convert trisodium phosphate to disodium phosphate (*A*), and to convert disodium phosphate to monosodium phosphate (*B*). Calculate and report percentage of trisodium phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, and percentage of disodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

$$\begin{aligned} \text{Per cent } \text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} &= \frac{A \times 3.8024}{\text{g. sample weighed}} \\ \text{Per cent } \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} &= \frac{(B - A) \times 3.5824}{\text{g. sample weighed}} \end{aligned}$$

Insoluble Matter, Iron, Aluminum, Calcium, and Magnesium.—Determine as described under analysis of sodium chloride (Chap. VIII).

Sulfate, Chloride.—Determine as described under analysis of sodium carbonate.

References

1. AMERICAN LEATHER CHEMISTS ASSOCIATION: Revision of Part of the Methods of the A. L. C. A., *J. Am. Leather Chem. Assoc.*, **22**, 567, 1927.
2. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS: "Official and Tentative Methods of Analysis," 2d ed., Washington, 1925.
3. ATKIN, W. R., and P. CHAMBARD: One-bath Chrome Liquors, *J. Soc. Leather Trades Chem.*, **8**, 504, 1924.
4. ATKIN, W. R., and F. C. THOMPSON: Analysis of Two-bath Chrome Liquors: Titration of Bichromate with Alkali, *J. Soc. Leather Trades Chem.*, **7**, 50, 1923.
5. BALDRACCO, G.: Analysis of Chrome Solutions for Tanning by the One-bath Process. *Boll. Ufficiale Roy. stat. sper. ind. pelli mat. concieri*, **2**, 17-19, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 688, 1924.
6. BLOCKEY, J. R.: Investigation of One-bath Chrome Liquors, *J. Soc. Leather Trades Chem.*, **2**, 205-212, 1918.
7. BURTON, D., and H. CHARLTON: Estimation of Sulfur Dioxide in Bleaching Extracts, *J. Intern. Soc. Leather Trades Chem.*, **10**, 326, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **23**, 112, 1927.
8. CHAMBARD, P.: Estimation of Chromic Oxide in Chrome Tanning Liquors, *Cuir*, **10**, 318, 1921.
9. CRAIG, T. J. I.: Volumetric Estimation of Sulfurous Acid, *J. Soc. Chem. Ind.*, **38**, 96T, 1919; abstracted in *J. Am. Leather Chem. Assoc.*, **14**, 480, 1919.
10. CUNNINGHAM, T. R., and T. R. McNEILL: Analysis of Chrome Ores, *Ind. Eng. Chem. (Anal.)*, **1**, 70-72, 1929.
11. GERMUTH, F. G.: Volumetric Determination of Aluminum in Aluminum Salts, *Ind. Eng. Chem.*, **19**, 144, 1927.
12. GRIFFIN, R. C.: "Technical Methods of Analysis," 1st ed., McGraw-Hill Book Company, Inc., New York, 1921.
13. GRASSER, G.: Analysis in Tanning Chemistry, *Collegium*, 224-227, 1921.
14. GRASSER, G.: Chemical Control in Iron Tanning, *ibid.*, 166, 1920; abstracted in *J. Am. Leather Chem. Assoc.*, **15**, 630, 1920.
15. GRASSER, G.: Determination of Chromium in the Presence of Organic Matter, *Z. Leder-Gerberei-Chem.*, **2**, 185-188, 1923.
16. HAN, J. E. S.: Iodimetric Determination of Chromium in Potash Chrome Alum, *J. Am. Leather Chem. Assoc.*, **24**, 124-129, 1929.
17. HARVEY, A.: "Practical Leather Chemistry," Crosby Lockwood & Son, London, 1920.
18. HARRISON, J. B. P., and M. F. CARROLL: Composition and Evaluation of Commercial Sodium Bisulfite, *J. Soc. Chem. Ind.*, **44**, 127T, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 226, 1925.
19. HEPBURN, J. R. I.: Determination of Carbon Dioxide in Carbonates, *Analyst*, **51**, 622, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 113, 1927.

20. INNES, R. F.: Decomposition of Sodium Peroxide Solutions by Means of Metallic Iron, *J. Soc. Leather Trades Chem.*, **6**, 5, 1922.

21. INNES, R. F.: Proposed Official Method for the Analysis of One-bath Chrome Liquors, *J. Intern. Soc. Leather Trades Chem.*, **13**, 111, 1929; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 438-439, 1929.

22. JAERVINEN, K. K.: Determination and Separation of Chromium, Iron, Aluminum, and Phosphorus, *Z. Anal. Chem.*, **75**, 1-27, 1928.

23. KANHAUSER, F.: Analysis of Chrome Materials in the Leather Industry, *Gerber*, **89**, 103, 1923.

24. KLABER, WILLIAM: One-bath Chrome Liquors and Their Analysis, *J. Am. Leather Chem. Assoc.*, **14**, 622, 1919.

25. KUBELKA, V., and J. WAGNER: Determination of Chromium in Used Chrome Liquors, *Collegium*, 257-266, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 656, 1927.

26. LAUFFMANN, R.: Influence of Iron and of Organic Matter on the Iodimetric Determination of Chromium, *Collegium*, 223-228, 1918; abstracted in *J. Am. Leather Chem. Assoc.*, **14**, 82, 1919.

27. LEVI, L. E. and E. V. MANUEL: "Tanners and Chemists Handbook," Privately printed, Milwaukee, Wis., 1909.

28. LEVI, L. E., and A. C. ORTHMANN: "Laboratory Manual," Pfister and Vogel Leather Co., Milwaukee, Wis., 1918.

29. LITTLE, E.: Analysis of One-bath Chrome Liquors, *J. Am. Leather Chem. Assoc.*, **11**, 61, 1916.

30. LITTLE, E., and E. M. DURAND: Analysis of Alkali and Carbonate Mixtures by Means of the Hydrogen Electrode, *J. Am. Leather Chem. Assoc.*, **20**, 19-31, 1925.

31. McCANDLISH, D.: Analysis of One-bath Chrome Liquors, *J. Am. Leather Chem. Assoc.*, **12**, 440-445, 1917.

32. MUELLER, E., and W. MESSE: Volumetric Determination of Chromium, *Z. Anal. Chem.*, **69**, 165-167, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 166, 1927.

33. PICKERING, J. E.: Analytical Determination of Basicity Figure, *J. Soc. Leather Trades Chem.*, **5**, 177-183, 1921.

34. PROCTER, H. R.: "Leather Chemists' Pocket Book," E. & F. N. Spon, London and New York, 1912; "Leather Industries Laboratory Book," E. & F. N. Spon, London and New York, 1908.

35. SCHLORLEMMER, K.: Estimation of Chromium in Chrome Salts, Liquors, Leather Ashes, and Residues, *Collegium*, 345, 371, 1917; *J. Soc. Leather Trades Chem.*, **2**, 57-58, 1918; abstracted in *J. Am. Leather Chem. Assoc.*, **13**, 223, 1918.

36. SCHLORLEMMER, K.: Estimation of Chromium in the Presence of Iron, *Collegium*, 145, 1918; abstracted in *J. Am. Leather Chem. Assoc.*, **13**, 610, 1918.

37. SCOTT, W. W., ed.: "Standard Methods of Chemical Analysis," 4th ed., revised, D. Van Nostrand Company, Inc., New York, 1927.

38. SMITH, C., and F. G. A. ENNA: Analysis of One-bath Chrome Liquors, *J. Soc. Leather Trades Chem.*, **2**, 213-214, 1918.

39. SOCIETY OF LEATHER TRADES CHEMISTS: Chrome Leather Analysis, Committee Report 1, *J. Soc. Leather Trades Chem.*, **3**, 194-197, 1919.

40. STIASNY, E., ed.: "Gerbereichemisches Taschenbuch," 2d ed., Theodore Steinkopff, Dresden and Leipzig, 1929.

41. THOMAS, A. W., and S. B. FOSTER: Acid Titration of Chrome Liquors, *J. Am. Leather Chem. Assoc.*, **16**, 61-63, 1921; Titration of Chrome Liquors by the Conductance Method, *ibid.*, **15**, 510-516, 1920.

42. THOMAS, A. W., and M. W. KELLY: Rapid Estimation of Chromium in Chrome Liquors by the Use of the Immersion Refractometer, *ibid.*, **15**, 665-668, 1920.

43. VAN HEURN, F. C.: Testing of Sodium Bisulfite, *J. Am. Leather Chem. Assoc.*, **14**, 530, 1919.

44. WILSON, J. A.: "The Chemistry of Leather Manufacture," 2d ed., vol. II, A. C. S. Mon. Ser., The Chemical Catalog Company, Inc., New York, 1929.

45. WOODROFFE, D.: Control of Chrome Liquors in the One-bath Tanning Process, Committee Report, *J. Intern. Soc. Leather Trades Chem.*, **9**, 480, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 225, 1926.

CHAPTER XI

FAT LIQUORING AND STUFFING MATERIALS AND LIQUORS

Fats and oils, and the products derived from them, are extremely important materials in leather manufacture. At some stage in its manufacture, nearly every kind of leather has some oil or grease incorporated in it, the amount, kind, and method of application varying with the type of leather. The principal methods of incorporating oil with leather are *fat liquoring*, which consists of drumming the leather with an emulsion of oil in water, *stuffing*, which consists of drumming wet skins with molten oil or grease, and *hand oiling*, which consists of swabbing oil on the surface of wet skins. The nature of the oil or grease employed varies with the process. In addition to true fats and oils, mineral oils, and paraffin, many secondary products derived from fats are employed, particularly in fat liquoring. The fats and related materials used by the tanner in fat liquoring, stuffing, or oiling may be classified as follows:

- I. Fixed, non-drying fats and oils.
- II. Mineral oil and paraffin.
- III. Moellons and *dégras*.
- IV. Sulfonated oils.
- V. Soaps.
- VI. Egg yolk.

This classification is purely one of convenience, based upon the methods used in analysis rather than upon constitution. Certain methods of analysis are common to all classes, but for each class special determinations, or modifications of procedure, are required. The analysis of waxes, of the so-called vulcanized oils, and of linseed oil, all of which are used to impart a coating to the leather surface, is dealt with under the analysis of finishing materials.

The purpose of analyzing materials used in fat liquoring is primarily to guard against the introduction of materials harmful to the leather or unsuited to the operation for which they are to

be used. This is vastly more important than the mere prevention of money loss due to the purchase of adulterated materials, for the use of an inferior oil or soap, or the wrong oil or soap regardless of its intrinsic value, may ruin leather worth many times the price of the entire shipment. The processes by which oil is incorporated with leather are as yet largely empirical. Each tanner has worked out a set of working conditions, employing certain materials in a certain way, that lead to the desired result, but only so long as no change is made in the materials employed. It is the purpose of chemical analysis to guarantee the constancy of properties of the materials used. In accomplishing this mission, each laboratory must work out a set of standards of its own, determining the composition and physical constants of specimens of each material that has proved satisfactory in use and the allowable variations.

ANALYSIS OF FIXED, NON-DRYING FATS AND OILS

This group includes all the natural, unfabricated fats and oils, except linseed and other drying oils, used by the tanner. All the members of this group are glycerides of the higher fatty acids. The fats and oils most commonly used in leather manufacture are listed in Table 49, (54) together with their physical and chemical constants. This list includes all the fats and oils which the authors have reason to believe to have been used in leather manufacture with reasonable success. Many other oils might be used if available in quantity at low prices. The constants given have been taken from International Critical Tables or from standard works on fat analysis (1, 23, 24). In general, the determinations may be assumed to have been made on the purest specimens obtainable. The corresponding values for commercial products may vary considerably from the figures given, particularly in the case of edible oils, in which cases only the poorer grades are used industrially. In Table 50 are given the average analytical figures obtained for neat's-foot, olive, cod, and cottonseed oils in the authors' laboratory during the past 10 years. As far as they go, these figures are probably more significant than those of Table 49, since they were determined on ordinary commercial products.

The analysis of fats and oils includes such tests as will show whether the material is what it is represented to be, whether it is adulterated, and whether it is in good condition. These tests

TABLE 49.—PHYSICAL AND CHEMICAL CONSTANTS OF FATS AND OILS

Material	Specific gravity at 15°C.	Congelation temperature, Centigrade	Saponification value	Iodine value	Maumene number	Per cent unsaponifiable	At degrees Centigrade		Viscosity (Saybolt universal) at degrees Fahrenheit
							Melting point of fatty acids	Solidification point of fatty acids (liter)	
Beef tallow..... (<i>Adipsa bovis</i>).....	0.943 0.952	27 38	193 200	35 46	42 46	38 47	
Bone fat..... (<i>Serum ossis</i>).....	0.914 0.916	15 17	185 198	46 56	0.5 1.8	41 44		
Castor oil..... (<i>Ricinus communis</i>).....	0.945 0.968	-18 -10	175 186	83 89	46 47	0.6	13	..	120
Coconut oil..... (<i>Cocos Butyracea</i>).....	0.926	14 22	246 268	6 10	21 27	0.1	24 27	21 25	45
Cod liver oil..... (<i>Gadus morhua</i>).....	0.921 0.931	-10 0	171 180	135 168	102 113	0.5 0.9	15 38	17 24	50
Corn oil..... (<i>Zea mays</i>).....	0.921 0.928	-20 -10	187 193	111 129	74 86	1.3 2.9	17 20	14 16	175
Cottonseed oil..... (<i>Gossypium sp.</i>).....	0.915 0.930	-13 +12	101 198	103 115	75 81	0.7 1.6	35 40	35	176
Dolphin oil..... (<i>Dolpinus globiceps</i>).....	0.908 0.930	-3 +5	187	100	...	2.0			
Herring oil..... (<i>Clupea harengus</i>).....	0.920 0.939	170 194	102 149	1.0 10.7	30 32		
Lard oil..... (<i>Oleum adipis</i>).....	0.913 0.919	-2 +10	193 198	62 80	40 47	0.6	33 38	27 33	
Monkaden oil..... (<i>Alou merliden</i>).....	0.923 0.933	-5 -4	189 193	138 185	169 ...	0.6 6.7	31	..	50
Mutton fat..... (<i>Adipsa oris</i>).....	0.937 0.953	32 41	192 197	35 61	33 54	40 49	

Neatsfoot oil (<i>Oleum patis bonis</i>)	0.913 0.918	- 2 +10	192 203	57 75	35 59	0.1 0.7	21 41	16 27	230 200	56 58
Olive oil	0.914	- 6	185	77	35	0.4	16	17		
(<i>Olea Europaea sativa</i>)	0.920	+ 2	196	91	52	1.0	30	26		
Palm kernel oil	0.950	26	290	10	25	20		
(<i>Elaeis guineensis</i>)	0.954	20	255	32	20	26		
Peanut oil	0.910	- 3	186	85	44	0.5	26	30		
(<i>Arachis hypogaea</i>)	0.926	+ 3	197	103	67	0.9	36	39		
Porpoise oil (body)	0.926	-16	195	110	50	3.7				
(<i>Deiphius phocaena</i>)	0.935	220	127	...	17.0				
Rapo seed oil	0.913	-10	107	94	50	0.6	18	12		
(<i>Brassica campestris</i>)	0.918	- 2	179	107	67	1.5	20	14		
Sardine oil	0.920	20	188	150	...	0.5	30	28		
(<i>Clupea pilchardus</i>)	0.934	22	200	183	...	1.4	35			
Seed oil	0.915	- 3	187	127	...	0.3	22			
(<i>Floct sp.</i>)	0.926	+ 3	190	159	...	1.4	23			
Sesame oil	0.921	- 6	188	103	61	0.9	25	23		
(<i>Sesamum indicum</i>)	0.924	- 4	193	117	69	1.3	35	32		
Shark oil (liver)	0.916	157	114	...	2.8	21			
(<i>Squalus maritima</i>)	0.919	164	141	...	15.2	22			
Sperm oil	0.878	- 5	120	80	51	37.0	13	..		
(<i>Physter macrocephalus</i>)	0.884	16	147	90	54	41.0	27			
Stearine (cotton seed)	0.919	16	105	88	27	35		
(<i>Gossypium sp.</i>)	0.923	22	...	103	45	51		
Tallow (liquid)	0.914	2	193	56	35		
(<i>Oleum adipis bovis</i>)	0.919	8	199	61	38		
Tallow (solid)	0.925	193	35	40		
(<i>Serum</i>)	0.950	198	45	50		
Whale oil	0.917	- 2	160	90	...	0.9	14	10		
(<i>Halena mydiorhus</i>)	0.924	0	202	146	..	4.0	27	21		
Wool fat	0.932	38	82	15	...	39.0	42			
(<i>Adipis lanu</i>)	0.973	40	130	29	...	51.8				

TABLE 50.—AVERAGE ANALYTICAL DATA FOR SOME OILS

	Cod	Cotton- seed	Neat's- foot	Olive
Specific gravity at 60°F.....	0.925	0.921	0.915	0.914
Viscosity at 100°C. (Dudley pipette method, water = 34 sec.), seconds.....	73	78	93	86
Cloud point, Fahrenheit.....	23	23	22	16
Iodine value (Hanus).....	137	106	74	83
Saponification value.....	167	197	196	192
Maumené value, degrees centi- grade.....	116	90	38	41
Free fatty acid (as oleic), per cent.....	13.36	0.12	1.36	4.08
Unsaponifiable matter.....	4.39	0.34	0.31	0.54
Unoxidized fatty acids.....	88.21	93.60	92.80	94.40
Iodine value.....	119	99	72	81
Melting point.....		27°C.	*	
Oxidized fatty acids.....	1.81	0.64	1.00	0.95

* Liquid at room temperature.

include (1) the estimation of certain constituents, such as unsaponifiable matter, free fatty acids, etc., (2) the measurement of certain physical constants, such as specific gravity, and (3) the determination of certain chemical constants or "numbers," depending upon the behavior of the material in chemical reactions. A very large number of such determinations have been proposed, especially for the purpose of detecting adulteration of food products, and many of them are of no particular value in the analysis of fats for leather making. The determinations described in this chapter will generally be found to give all information needed concerning an oil or a fat to be used in the tannery. For such determinations as are not given, the large textbooks dealing with fats and oils, such as those of Allen (1) and Gnamn (23), or the methods of analysis of the Association of Official Agricultural Chemists (8) should be consulted.

SPECIFIC GRAVITY

Specific Gravity at 60°F.: Oils Liquid at 60°F.—Determine specific gravity by means of the Westphal balance as follows: Fill a suitable cylinder with oil and cool to a temperature slightly below 60°F. by immersing the

cylinder in cold water. Stir with a thermometer, taking care not to entrap air bubbles in the oil. Adjust the balance by means of the leveling screw so that the point on the beam is exactly opposite the point on the fixed part. Suspend the plummet in the oil, and add weights to bring the instrument into balance. Note the temperature recorded by the thermometer in the plummet, and adjust the weights to maintain balance as the temperature of the oil rises, taking the reading when the temperature is exactly 60°F. (47).

Young's gravitometer, which works on the same principal, is rather more convenient than the Westphal balance. This instrument permits the second and third decimal places of specific gravity to be read by means of a pointer and scale.

Specific Gravity at 60°F.: Fats Solid at 60°F. (Based on A. S. T. M. Standard Method (D 70-27) (7)).—Clean, dry, and weigh a pycnometer like that shown in Fig. 74, consisting of a straight-sided weighing bottle with solid glass stopper, concave on the inside, and pierced with a hole about 1.6 mm. in diameter. Melt about 15 g. of fat on the steam bath, heat the pycnometer to the same temperature, and pour the melted material into the pycnometer until it is about half full, taking care that no material touches the sides above the final level of the fat and that no air bubbles are entrapped. Let the fat cool spontaneously at room temperature, and allow it to stand several hours after solidification is complete. Weigh the pycnometer (stoppered) and fat. Fill the remaining space in the pycnometer with recently boiled distilled water at about 75°F., and insert the stopper, taking care that no air is trapped and that the hole in the stopper is full to the top. Immerse the pycnometer completely in a beaker of recently boiled distilled water at about 75°F., cool, and note the temperature. When the water is at exactly 60°F., remove the pycnometer, wipe dry quickly with a clean cloth, and weigh. Previous to the determination, determine the weight of the pycnometer filled with water only in the same way. Calculate specific gravity of the fat as follows:



FIG. 74.—
Pycnometer
for determin-
ing specific
gravity of
fat

Let

- a = weight of pycnometer empty
- b = weight of pycnometer filled with water
- c = weight of pycnometer and fat
- d = weight of pycnometer filled with fat and water

Then specific gravity of fat equals weight of fat divided by weight of water occupying the same volume, or

$$\text{sp. gr.} = \frac{c - a}{b - a}$$

Flotation Method.—See analysis of waxes (Chap. XII).

Specific Gravity at 100°C.: Materials Solid at Room Temperature.—Determine by means of the Westphal balance, using a special plummet and surrounding the oil cylinder with boiling water during the determination (47).

MELTING POINT

The melting point of many fats and oils is not very sharply defined, the change from the solid to the liquid state taking place gradually over a range of several degrees. The exact temperature taken as the melting point depends upon the method employed. In the capillary tube method it is that temperature at which the column of fat in the tube becomes wholly transparent. The observed melting point is also affected by the previous history of the specimen and the rate of heating. If the fat is melted and cooled suddenly below the solidification point, it must be allowed to stand for some time to allow stresses created by the cooling to readjust themselves, or else the observed melting point will be too low; if the solid fat is heated faster than the prescribed rate, the observed melting point is likely to be too high. The melting point of the fatty acids liberated from a fat is rather more characteristic than that of the fat itself. Instead of the melting point, the solidification point or "titer test" of the fatty acids may be determined. Solidification points of fats generally are about 2° lower than their melting points.

Capillary Tube Method (Based on Official Method of the A. O. A. C.) (8).—Melt the fat or fatty acid. Draw into a thin-walled capillary tube of about 0.5 mm. diameter (made by drawing out a thin-walled test tube in the blast flame) a column of fat about as long as the thermometer bulb. Seal one end of the capillary in the blast flame. Place the capillary on ice overnight. Attach the capillary to the bulb of a thermometer graduated in 0.2°C. units, and immerse it in a large test tube containing water at ice-box temperature (or at least 5° below the approximate melting point of the fat, if this is known). Surround the test tube with a beaker of water at the same temperature. Stir the water mantle, preferably by a gentle stream of air. Heat the outer beaker over a flame so regulated that the rise in temperature is not greater than 1°C. per minute. Observe the column of fat in the capillary, and take the point at which it becomes transparent as the melting point.

If the material is liquid at ice-box temperature, report: "melting point: liquid at ———°C."

Official Method of the American Leather Chemists Association for Melting Point of Hard Greases (6). *Thermometer*.—Use a thermometer graduated on the centigrade scale and having a bulb not less than 0.625 or more than 0.750 in. long.

Determination.—Bring the grease to a temperature approximately 10°C. above its melting point, dip the thermometer into the melted grease to the depth of its bulb, remove after 5 sec., rotate slowly in the vertical position, and before the grease quite solidifies remove the excess drop of grease on the bottom of the bulb by touching it with the hand. After letting the thermometer stand overnight, place it in a test tube 6 by 1 in. and cork

loosely, so that the bulb is 1 in. from the bottom of the tube. Suspend the test tube and thermometer in a beaker of water, with the bottom of the test tube 1 in. above the bottom of the beaker. Gradually raise the temperature of the water to about 15°C. below the probable melting point, and then raise the temperature not less than 1°C. or more than 1.5°C. per minute until a drop of clear grease forms on the bottom of the bulb. The temperature at which this occurs represents the melting point.

Titer Test (Solidification Point of Fatty Acids) of Hard Greases: Official Method of the A. L. C. A. (6). *Titer Tube.*—Use a titer tube 25 mm. in diameter and 100 mm. in length and of glass about 1 mm. thick.

Determination.—Saponify 75 g. of sample in a metal dish with 60 ml. of 30-per cent sodium hydroxide solution (36° Bé.) and either 75 ml. of 95-per cent alcohol by volume or 120 ml. of water. Evaporate to dryness over a very low flame or over a heated iron or asbestos plate, stirring constantly to prevent scorching. Dissolve the dry soap in 1 l. of boiling water, and if alcohol has been used, boil for 40 min. to remove it, adding enough water to replace that lost in boiling. Add 100 ml. of 30-per cent sulfuric acid (25° Bé.) to liberate the fatty acids, and boil until they form a clear, transparent layer. Wash the fatty acids with boiling water until free from sulfuric acid, collect them in a small beaker, place on a steam bath until the water settles and the fatty acids are clear, then decant into a dry beaker, filter, using a hot water funnel, and dry the fatty acids for 20 min. at 100°C. When dried, cool to 15 or 20°C. above the expected titer and transfer to the titer tube. Place the tube in a 16-oz. wide-mouth bottle of clear glass, 70 by 150 mm., fitted with a perforated stopper to hold the tube rigidly in position. Suspend a thermometer, with graduations of 0.1°C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for 30 sec. Then allow the thermometer to hang quietly, with its bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids. For fats having a titer above 30°C. determine the titer in a surrounding temperature of 20°C. For other fats determine the titer in a surrounding temperature 10° below the titer of the sample.

Test the fatty acids for complete saponification as follows: Place 3 ml. in a test tube, add 15 ml. of 95-per cent alcohol by volume, bring to boiling, and add the same volume of concentrated ammonium hydroxide. A clear solution results if saponification was complete.

VISCOSITY

Viscosity, which is so important a characteristic of lubricating oils, is not in itself of much importance in oils used in leather manufacture, except for such viscous materials as vulcanized oils. Otherwise, the determination of viscosity merely provides one characteristic by which uniformity of successive shipments of an oil may be judged. Viscosity is generally measured by determining the time of outflow of a definite volume of oil, at a specified temperature, from an orifice under specified conditions. Results are reported either in seconds for the particular type of instru-

ment or as relative viscosity, taking that of water as unity. Many forms of viscosimeters have been devised. The Saybolt instrument has been adopted as standard by the American Society for Testing Materials (7). A simpler, though much less precise instrument is the Dudley or "Pennsylvania Railroad" pipette. The use of both these instruments is described below. Another method of measuring viscosity consists of determining the time required for an air bubble to rise through a column of the oil. Similar to this method in principle is the falling ball method, in which the time required for a steel ball to fall through a measured column of liquid is determined. This method is used for determining the viscosity of nitrocellulose solutions and is described in Chap. XII.

STANDARD METHOD OF THE A. S. T. M. (D 88-26) (7)

1. *a.* Viscosity shall be determined by means of the Saybolt Universal or Saybolt Furol viscosimeter.

b. In general, the Saybolt Universal viscosimeter shall be used for lubricants and the Saybolt Furol viscosimeter for fuel oils and other oils of similar viscosity.

TABLE 51.—DIMENSIONS OF OIL TUBES
Centimeters

Dimension	Saybolt Universal viscosimeter			Saybolt Furol viscosimeter		
	Mini- mum	Nor- mal	Maxi- mum	Mini- mum	Nor- mal	Maxi- mum
Inside diameter of outlet tube.....	0.1750	0.1765	0.1780	0.313	0.315	0.317
Outside diameter of outlet tube at lower end.....	0.28	0.30	0.32	0.40	0.43	0.46
Length of outlet tube*.....	1.215	1.225	1.235	1.215	1.225	1.235
Height of overflow rim above bottom of outlet tube*.....	12.40	12.50	12.60			12.60
Outside diameter of overflow rim, at the top†.....	†		3.30	†		3.30
Diameter of container*.....	2.955	2.975	2.995	2.955	2.975	2.995
Depth of cylindrical part of container*.....	8.8					
Diameter of container between bottom of cylindrical part of container and top of outlet tube*.....	0.9			0.9		

* This dimension is identical in the Saybolt Universal and the Saybolt Furol instruments.

† The minimum value shall preferably be not less than 3.2 cm.

‡ The section of overflow rim shall be bounded by straight lines, except that a fillet is permissible at the junction with the bottom of the gallery.

c. The Saybolt Universal viscosimeter shall not be used for times of flow less than 32 sec.

2. *a.* The Saybolt viscosimeters (see Fig. 75) are made entirely of metal. The oil tube *A* is fitted at the top with an overflow cup *B*, and the tube is surrounded by a bath. At the bottom of the oil tube is a small outlet tube through which the oil to be tested flows into a receiving flask (Fig. 76) whose capacity at 20°C. (68°F.) to a mark on its neck is 60 ± 0.15 cc. The outlet tube is of hard and non-corrosive metal such as stainless steel, monel

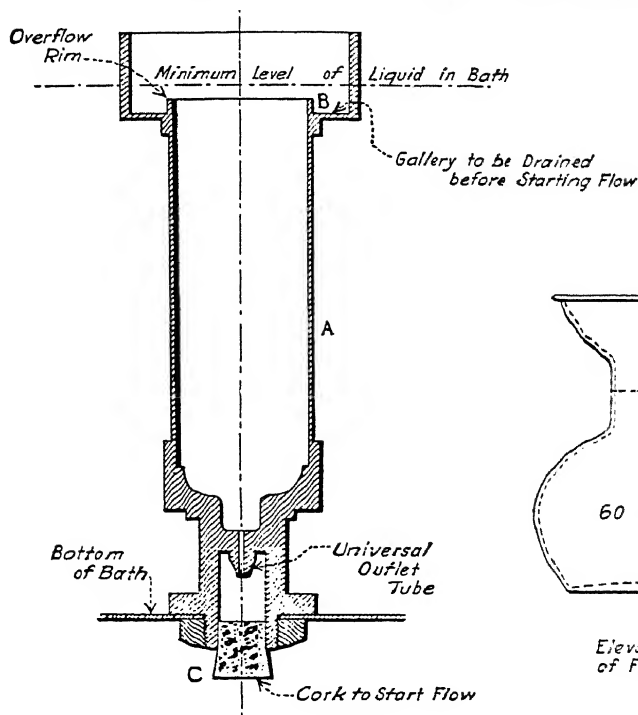


Fig. 75.—Sectional view of standard oil tube.

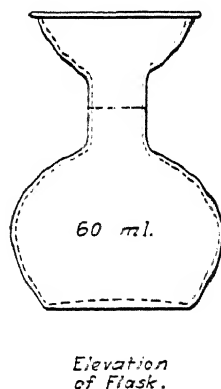


Fig. 76.—Receiving flask. (This type of flask is recommended as convenient and durable.)

metal, etc. The inside diameter of the neck of the flask, at the level where the graduation mark is placed, is 0.8 to 1.1 cm. The lower end of the outlet tube is enclosed by a larger tube, which when stoppered by a cork *C* acts as a closed air chamber and prevents the flow of oil through the outlet tube until the cork is removed and the test started. A looped string may be attached to the lower end of the cork as an aid to its rapid removal. The

temperatures in the oil tube and in the bath are shown by thermometers. The bath may be heated by any suitable means. The oil tube shall be thoroughly cleaned, and all oil entering the oil tube shall be strained through a 100-mesh wire strainer. A stop watch shall be used for taking the time of flow of the oil, and a pipette shall be used for draining the overflow cup.

b. The oil tubes, which may be standardized by the U. S. Bureau of Standards, shall conform to the dimensions given in Table 51. The time of flow shall be within ± 1 per cent of the time as obtained with the Bureau of Standards' master tube.

c. The bath and oil tube thermometers shall conform to the following requirements. They cover 2 sets of 4 thermometers each, 1 set being graduated in Fahrenheit degrees and the other set in centigrade degrees, the ranges being chosen to include the temperatures commonly used in testing.

Type.—Etched stem, glass.

Liquid.—Mercury.

RANGES AND SUBDIVISIONS

Range, °F.	Subdivision, °F.	For tests made at, °F.
66 to 80	0.2	77
94 to 108	0.2	100
120 to 134	0.2	122 and 130
204 to 218	0.2	210
Range, °C.	Subdivision, °C.	For tests made at, °C.
19 to 27	0.1	25
34 to 42	0.1	40
49 to 57	0.1	50
95 to 103	0.1	100

Total Length.—252 to 256 mm. (9.92 to 10.08 in.).

Stem.—Plain front, enamel back, suitable thermometer tubing. Diameter, 6 to 7 mm. (0.236 to 0.275 in.). The stem shall preferably be made with an enlargement not less than 4 nor more than 7 mm. (0.16 to 0.28 in.) in length, having a diameter 2 to 3 mm. (0.08 to 0.12 in.) greater than that of the stem, the bottom of the enlargement being 114 mm. (4.5 in.) above the bottom of the bulb.

Bulb.—Corning normal or equally suitable thermometric glass. Length, 25 to 35 mm. (1.0 to 1.4 in.). Diameter, not less than 5 mm. (0.197 in.) and not greater than that of stem.

Distance to Lowest Specified Graduation from Bottom of Bulb.—135 to 150 mm. (5.3 to 5.9 in.).

Distance to Highest Specified Graduation from Top of Stem.—20 to 35 mm. (0.8 to 1.4 in.).

Contraction Chamber.—To be of long narrow type, top to be not more than 60 mm. (2.36 in.) above bottom of bulb, mercury to stand in contraction chamber at 32°F. (0°C.).

Expansion Chamber.—To permit heating the thermometer 90°F. (50°C.) above highest temperature on scale, and in all cases to permit heating to 212°F. (100°C.).

Filling above Mercury.—Nitrogen gas.

Top Finish.—Glass ring.

Graduation.—All lines, figures, and letters clear cut and distinct. The first and each succeeding 1°F. (0.5°C.) line to be longer than the remaining lines. Graduations to be numbered at each multiple of 2°F. (1°C.).

Immersion.—Total.

Special Marking.—A. S. T. M. Viscosity test points to be numbered in full figures and in red, other graduations and figures in black. A serial number and the manufacturer's name or trade-mark shall be etched on the stem.

Scale Error.—The error at any point of the scale shall not exceed 0.2°F.

Standardization.—The thermometers are to be standardized for the condition of total immersion. Correction for emergent stem shall not be applied.

Case.—Each thermometer shall be supplied in a suitable case on which shall appear the marking, "A. S. T. M. Saybolt viscosimeter thermometer" and the range.

TEMPERATURE OF TESTING

3. *a.* With the Saybolt viscosimeter, determinations shall be made at 100°F. (37.8°C.), 130°F. (54.4°C.), or 210°F. (98.9°C.).

b. With the Saybolt Furol viscosimeter, determinations shall be made at 122°F. (50°C.).

c. Viscosities shall be expressed as seconds, Saybolt Universal (or Saybolt Furol), being the time in seconds for the delivery of 60 cc. of oil.

d. Fuel oils and other oils of similar viscosity showing a time of less than 25 sec., Saybolt Furol, at 122°F., shall be tested on the Saybolt Universal at 122°F. Oil showing a time of less than 32 sec., Saybolt Universal, at 122°F., shall be measured in the Saybolt Universal at 100°F. (37.8 C.) These methods of test do not apply to fuels having a viscosity at 100°F. of less than 32 sec. Saybolt Universal, which are not considered to be fuel oils.

PROCEDURE

4. In tests at 100 and 130°F. (37.8 and 54.4°C.) the bath temperature throughout the test shall not vary more than $\pm 0.1^\circ\text{F.}$ (0.06°C.) from the predetermined temperature which will maintain thermal equilibrium as long as the oil is well stirred with the thermometer. In tests at 210°F. (98.9°C.) a variation of $\pm 0.2^\circ\text{F.}$ (0.11°C.) is permitted.

Any construction of bath may be employed provided the bath temperature necessary to maintain thermal equilibrium (while the oil in the oil tube is well stirred by the oil tube thermometer) is not in excess of 100.25, 122.35, 130.50, and 212.00°F. (37.9, 50.2, 54.7 and 100.00°C.), respectively, for the standard temperatures previously mentioned. The level of the bath liquid shall not be lower than 0.5 cm. above the overflow rim of the oil tube. In tests at 210°F. (98.9°C.) the water bath shall be vigorously stirred and may be heated by the direct injection of steam near the bottom of the bath. A bath of other suitable liquid may be used provided it is heated and stirred.¹ The heating and stirring of the bath may be accomplished by any suitable means, provided the source of heat is not less than the following distances from any part of the oil tube: 2 in. (5 cm.) with an external heater, 1¼ in. (3 cm.) with an immersion heater. Viscosity determinations shall be made in a room free from draughts and from rapid changes in temperature. The room temperature shall be between 68 and 86°F. (20 and 30°C.).²

All oil introduced into the oil tube, either for cleaning or for test, shall first be passed through the strainer.

To make the test, heat the oil to the necessary temperature and clean out the oil tube. Pour some of the oil to be tested through the cleaned tube. Insert the cork stopper into the lower end of the air chamber at the bottom of the oil tube, sufficiently to prevent the escape of air but not to touch the small outlet tube.

Heat the oil to be tested, outside the viscosimeter, to slightly but not more than 3°F. (1.7°C.) above the temperature at which the viscosity is to be determined, and pour it into the oil tube until it ceases to overflow into the overflow cup. By means of the oil tube thermometer, keep the oil in the oil tube well stirred, and also stir well the liquid in the bath. It is extremely important that the temperature of the bath be maintained constant during the entire time consumed in making the test. After the temperature of the bath and of the oil in the oil tube have been constant for 1 min. at the desired temperatures, withdraw the oil tube thermometer, quickly remove the surplus oil from the overflow cup by means of a pipette³

¹ For example, the bath liquid may be water, to which glycerin or salt has been added. In ordinary routine testing it is frequently desirable to employ oil as bath medium. This is allowable provided the temperature of the oil bath is adjusted so that the necessary condition of thermal equilibrium is maintained. It is usually necessary to maintain the oil bath at slightly higher temperatures than are necessary when water is the bath medium. Oil bath temperatures will need to be from 0.1 to 0.2°F. (0.06 to 0.11°C.) higher for tests at 100°F. (37.8°C.) and 1.5 to 2.0°F. (0.85 to 1.11°C.) higher for tests at 210°F. (98.9°C.) than the corresponding water bath temperatures.

² These limits are necessary for extreme accuracy in standardization and referee tests, but for routine purposes the use of higher temperatures up to 100°F. (37.8°C.) will not ordinarily cause an error of more than 1 per cent.

³ It is recommended that the tip of the pipette should be about 2 mm. inside, and about 3 mm. outside diameter, and great care should be exercised to avoid touching the overflow rim while draining the overflow cup.

so that the level of the oil in the overflow cup is below the level of the oil in the oil tube proper; place the 60-cc. flask (Fig. 76) in position so that the stream of oil from the outlet tube will strike the neck of the flask so as to avoid foam. Snap the cork from its position, and at the same instant start the stop watch. Stir the liquid in the bath during the run, and carefully maintain it at the previously determined proper temperature. Stop the watch when the bottom of the meniscus of the oil reaches the mark on the neck of the receiving flask.

The time in seconds for the delivery of 60 cc. of oil is the Saybolt Universal (or Saybolt Furo) viscosity of the oil at the temperature at which the test is made.

With proper attention to details of methods of procedure, duplicate results should not differ from each other by more than 1 per cent.

Dudley Pipette Method.—The instrument is a glass pipette of ordinary shape, having marks on the stem just above and just below the bulb. The volume contained between the two marks is 100 cc., and the orifice is of such size that 100 cc. of water at 100°F. contained between the marks is delivered in 34 sec.

Clean the pipette with hot soap solution or with chromic acid, rinse several times with distilled water, then with alcohol and with ether, and dry by passing a current of air through the pipette. If the oil contains sediment, filter about 150 cc. through dry filter paper. Heat the filtered oil to about 102°F. Fill the pipette by suction until the meniscus is a little above the upper mark. Support the pipette vertically in a funnel rack. Remove the thumb from the pipette, and note the time required for the meniscus to travel from the upper to the lower mark. Reheat the oil to 100°F., and repeat the determination, until 2 measurements agreeing to the nearest whole second are obtained.

Report "viscosity at 100°F. (water = 34 sec.) = ——— sec."

Air Bubble Method.—The apparatus consists of a flat-bottom tube having a diameter of 11.3 mm.¹ At the top of the tube 2 lines are etched, the top one indicating the depth to which the cork should be inserted and the bottom one the point to which the tube should be filled with oil. The bottom of the meniscus must be on this line. The size of the air bubble is therefore determined by the distance between the lines, and great care must be exercised in filling the tube accurately.

Fill the tube with oil, making sure that all small air bubbles are out of the oil before making the determination. Cork the tube, and immerse it (standing vertically) in water at 77°F. for at least 10 min. The temperature must be carefully regulated, as a difference of 1° may make a difference of 5 per cent in the reading. Remove the tube from the bath, reverse the tube quickly, and measure with a stop watch the time for the bubble to travel to the other end of the tube. Hold the tube vertical during the transit of the bubble. The end point is that moment when the bubble ceases to move, that is, when it touches the end of the tube, not that when all oil has drained away from the end of the tube. Let the tube stand after the determination until all oil has drained away, then reverse the tube, and repeat the measurement. Continue until readings that check are obtained.

¹ Supplied by R. P. Cargille, 26 Cortlandt Street, New York City.

CLOUD POINT AND POUR POINT

When an oil is slowly cooled, a point is reached at which solid glycerides separate, making the oil cloudy. The temperature at which this occurs is called the cloud point. On cooling still more, the oil congeals and will no longer flow when the bottle in which it is contained is tipped on its side. The temperature at which the oil ceases to flow is known as the pour point, according to the standard method of the A. S. T. M. Another definition of pour point is that temperature at which the oil flows again after having been congealed.

The importance of a low cloud point in oils to be used on leather lies in the fact that high cloud point indicates the presence of glycerides that may solidify on the surface of the leather in the form of a spew. The determination of cloud and pour point is most important in the case of neat's-foot oil, which is pressed from solid beef fat. Most tanners insist upon being supplied with cold-pressed oil, which should have a cloud point not higher than 20°F.

In the author's judgment, the information afforded by the cloud point can be obtained much more reliably from the determination of melting point of free fatty acids obtained from the oil. Most fats incorporated with leather are hydrolyzed in time, and the solidification temperature of the liberated fatty acids is a much more reliable criterion of freedom from tendency to spew than is the cloud point.

At present, no method for determining cloud and pour points is accepted as official by the A. L. C. A. Committee work (39) has shown, however, that the standard method of the A. S. T. M. (7) for determining cloud and pour points of lubricating oils is adaptable to the oils used in leather manufacture. This method is given below. The authors prefer a slightly different method, for reasons stated below. A very convenient method has been described by Orthmann and Arner (42).

STANDARD METHOD OF THE A. S. T. M., D 97, 28 (7)

1. a. The cloud point of a petroleum oil is that temperature at which paraffin wax or other solid substances begin to crystallize out or separate from solution when the oil is chilled under certain definite specified conditions.

b. The pour point of a petroleum oil is the lowest temperature at which this oil will pour or flow when it is chilled without disturbance under certain definite specified conditions.

2. *a*. The test for cloud point shall be used only for oils which are transparent in layers $1\frac{1}{2}$ in. thick.

b. The test for pour point shall be used for all other petroleum oils and may be used for oils on which the test for cloud point is permitted.

APPARATUS (SEE FIG. 77)

3. The test jar *a* shall be of clear glass, cylindrical form, flat bottom, approximately $1\frac{3}{16}$ to $1\frac{5}{16}$ in. in inside diameter and $4\frac{1}{2}$ to 5 in. high. An ordinary 4-oz. oil sample bottle may be used if it is within the above specifications and no test jar is available.

The thermometer *b* shall conform to the requirements of the following specifications:

These specifications cover a special thermometer graduated in either centigrade or Fahrenheit degrees as specified, the ranges being -38 to $+50^{\circ}\text{C}$. or -36 to $+120^{\circ}\text{F}$., respectively.

Type.—Etched stem, glass.

Liquid.—Mercury.

Range and Subdivision: -38 to $+50^{\circ}\text{C}$. in 1°C . or -36 to $+120^{\circ}\text{F}$. in 2°F .

Total Length: 220 to 224 mm. (8.69 to 8.81 in.).

Stem.—Plain front, enamel back, suitable thermometer tubing. Diameter, 7.0 to 8.0 mm. (0.28 to 0.31 in.).

Bulb.—Corning normal or equally suitable thermometric glass. Length, not over 9.5 mm. (0.37 in.). Diameter, not greater than stem.

Distance to: -38°C .- or -36°F .-Line from Bottom of Bulb: 120 to 130 mm. (4.73 to 5.12 in.).

Distance to: $+49^{\circ}\text{C}$.- or $+120^{\circ}\text{F}$.-Line from Top of Thermometer: 19 to 25 mm. (0.75 to 0.98 in.).

Expansion Chamber.—To permit heating to 100°C . or 212°F .

Filling above Mercury.—Nitrogen gas.

Top Finish.—Plain.

Graduation.—All lines, figures, and letters clear cut and distinct. at multiples of 5°C . or 10°F . to be longer than the remaining lines. Graduations to be numbered at each multiple of 10°C . or 20°F .

Immersion: 108 mm. or $4\frac{1}{4}$ in. The words "10S-mm. immersion" on centigrade thermometers or " $4\frac{1}{4}$ -in. immersion" on Fahrenheit ther-

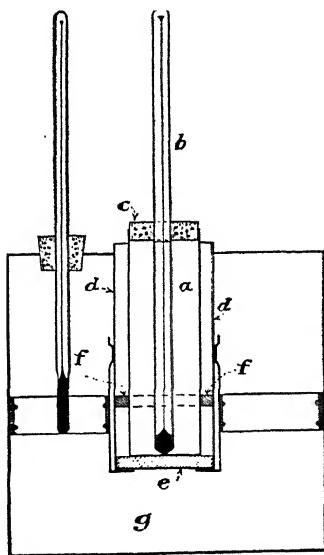


FIG. 77.—Apparatus for cloud and pour test (as assembled for cloud test).

monometers and a line around the stem 108.0 mm. or 4.25 in. above the bottom of the bulb shall be etched on the thermometer.

Special Marking.—"A. S. T. M. cloud and pour," a serial number, and the manufacturer's name or trade-mark shall be etched on the stem.

Scale Error.—The error at any point of the scale, when the thermometer is standardized as provided below, shall not exceed 0.5°C. or 1°F.

Standardization.—The thermometer shall be standardized at the ice point and at intervals of approximately 20°C. or 40°F. for 108-mm. or 4 $\frac{1}{4}$ -in. immersion and for an average temperature of 21°C. or 70°F. for the emergent mercury column.

Case.—The thermometer shall be supplied in a suitable case on which shall appear the marking: "A. S. T. M. cloud and pour, -38 to +50°C.," or "A. S. T. M. cloud and pour, -36 to +120°F.," according to the type of thermometer.

NOTE.—For the purpose of interpreting these specifications the following definitions apply:

The total length is the overall length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

[AUTHOR'S NOTE.—Specifications for a similar thermometer covering the range -70 + 70°F. have been omitted.]

5. The cork *c* shall fit the test jar and shall be bored centrally to take the test thermometer.

6. The jacket *d* shall be of glass or metal, shall be water-tight, of cylindrical form, flat bottom, about 4 $\frac{1}{2}$ in. deep, with inside diameter $\frac{3}{8}$ to $\frac{1}{2}$ in. greater than outside diameter of the test jar.

7. A disk of cork or felt *e* $\frac{1}{4}$ in. thick and of the same diameter as the inside of the jacket will be required.

8. The ring gasket *f* shall be about $\frac{3}{16}$ in. thick and made to fit snugly around the outside of the test jar and loosely inside the jacket. This gasket may be made of cork, felt, or other suitable material elastic enough to cling to the test jar and hard enough to hold its shape. The purpose of the ring gasket is to prevent the test jar from touching the jacket.

9. The cooling bath *g* shall be of a type suitable for obtaining the required temperatures. The size and shape of the bath are optional, but a support suitable for holding the jacket firmly in a vertical position is essential. For determination of very low pour points, a smaller insulated cooling bath may be used and the test jar placed directly in it. The required bath temperatures may be maintained by refrigeration if available, otherwise by suitable freezing mixtures.

NOTE.—The freezing mixtures commonly used are as follows:

For temperatures down to 50°F., ice and water.

For temperatures down to 10°F., crushed ice and sodium chloride.

For temperatures down to -15°F., crushed ice and calcium chloride crystals.

For temperatures down to -70°F., solid carbon dioxide and acetone or gasoline.

PROCEDURE

10. Cloud Point.—The oil to be tested shall be brought to a temperature at least 25°F. above the approximate cloud point. Moisture, if present, shall be removed by any suitable method, as by filtration through dry filter paper until the oil is perfectly clear, but such filtration shall be made at a temperature at least 25°F. above the approximate cloud point.

The clear oil shall be poured into the test jar *a* to a height of not less than 2 nor more than $2\frac{1}{4}$ in. The test jar may be marked to indicate the proper level.

The test jar shall be tightly closed by the cork *c* carrying the test thermometer *b* in a vertical position in the center of the jar with the thermometer bulb resting on the bottom of the jar.

The disk *e* shall be placed in the bottom of the jacket *d*, and the test jar with the ring gasket *f* 1 in. above the bottom shall be inserted into the jacket. The disk, jacket, and inside of jacket shall be clean and dry.

The temperature of the cooling bath *g* shall be adjusted so that it is below the cloud point of the oil by not less than 15 nor more than 30°F., and this temperature shall be maintained throughout the test. The jacket, containing the test jar, shall be supported firmly in a vertical position in the cooling bath so that not more than 1 in. of the jacket projects out of the cooling medium.

At each test thermometer reading which is a multiple of 2°F., the test jar shall be removed from the jacket, quickly but without disturbing the oil, inspected for cloud, and replaced in the jacket. This complete operation shall require not more than 3 sec.

When such inspection first reveals a distinct cloudiness or haze in the oil at the bottom of the test jar, the reading of the test thermometer, corrected for error if necessary, shall be recorded as the cloud point.

11. Pour Point.—The oil shall be poured into the test jar *a* to a height of not less than 2 nor more than $2\frac{1}{4}$ in. The jar may be marked to indicate the proper level. When necessary, the oil shall be heated in a water bath just sufficiently for pouring into the test jar.

The test jar shall be tightly closed by the cork *c* carrying the test thermometer *b* in a vertical position in the center of the jar with the thermometer bulb immersed so that the beginning of the capillary shall be $\frac{1}{8}$ in. below the surface of the oil.

Heat without stirring to a temperature of 115°F. in a bath maintained at not higher than 118°F. The oil shall then be cooled to 90°F. in air or in a water bath approximately 77°F. in temperature. Oils with which the low cloud and pour test thermometer can be used from the beginning of the test shall be cooled to 60°F. in any convenient manner before the thermometer is placed in position.

The disk *e* shall be placed in the bottom of the jacket *d*, and the test jar, with the ring gasket *f* 1 in. above the bottom, shall be inserted into the jacket. The disk, gasket, and inside of jacket shall be clean and dry.

After the oil has cooled enough to allow the formation of paraffin wax crystals, great care shall be taken not to disturb the mass of the oil nor to permit the thermometer to shift in the oil. Any disturbance of the spongy network of wax crystals will lead to low and fictitious results.

The temperature of the cooling bath *g* shall be adjusted so that it is below the pour point of the oil by not less than 15 nor more than 30°F., and this temperature shall be maintained throughout the test. The jacket, containing the test jar, shall be supported firmly in a vertical position in the cooling bath so that not more than 1 in. of the jacket projects out of the cooling medium.

Beginning at a temperature 20°F. before the expected pour point, at each test thermometer reading which is a multiple of 5°F., the test jar shall be removed from the jacket carefully and shall be tilted just enough to ascertain whether there is a movement of the oil in the test jar. The complete operation of removal and replacement shall require not more than 3 sec. As soon as the oil in the test jar does not flow when the jar is tilted, the test jar shall be held in a horizontal position for exactly 5 sec., as noted by a stop watch or other accurate timing device, and observed carefully. If the oil shows any movement under these conditions, the test jar shall be immediately replaced in the jacket and the same procedure repeated at the next temperature reading 5°F. lower.

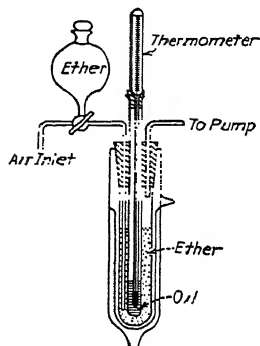


FIG. 78.—Ether evaporation apparatus for cooling oil in determining cloud and pour points.

The test shall be continued in this manner until a point is read at which the oil in the test jar shows no movement when the test jar is held in a horizontal position for exactly 5 sec. Certain lubricating oils tend to move as a whole and should be very closely observed. The reading of the test thermometer at this temperature, corrected for error if necessary, shall be recorded. The pour point shall be taken as the temperature 5°F. above this solid point.

Author's Method.—Heat the oil momentarily to 150°C. to expel water. Filter *hot* into a dry, hot test bottle. Proceed as in the A. S. T. M. method, but stir the oil with the thermometer each time the test jar is removed from the cooling bath, taking care not to churn any air bubbles into the oil. As oil conducts heat poorly, a cloud generally forms first at the bottom and sides of the jar, but disappears on stirring. Take the cloud point as that temperature at which a cloud forms in the oil near the thermometer, and does not disappear upon stirring.

Method of Orthmann and Arner (42).—This method differs from that of the A. S. T. M. only in the arrangement for cooling. The apparatus¹ used is shown in Fig. 78. It consists of a 3-walled glass Dewar flask which is filled three-fourths full with ether. Into this bath is placed a test tube, 23 cm. long and 15 mm. inside diameter, filled with oil to a mark 30 mm. from the bottom. The tube carries a thermometer fitted into it through a rubber stopper. Air is dried by passing through a calcium chloride tube and is sucked through the ether by means of a pump. The evaporation of

¹ Manufactured by Carl Stellung, Rodingmarkt 81, Hamburg II, Germany.

the ether produces the desired temperature lowering, and the rate of fall can be varied by varying the rate of flow of air.

Fill the tube with oil at room temperature. Start the pump, and watch for the appearance of cloud as the temperature falls. It is not necessary to remove the tube from the apparatus to make the observations. Record the cloud point temperature. Continue cooling until the oil is at a temperature about 10°C. above the expected pour point. Tilt the entire apparatus, and note whether or not the oil flows. Repeat after each degree fall in temperature. When the oil shows no apparent movement, remove the tube from the jar, lay it on its side, and note whether any movement occurs. If movement is observed, return the tube to the jar, and repeat the test for each degree fall in temperature until movement takes place when the tube is laid on its side. Report a temperature 1°C. above this temperature as pour point.

WATER

Water is not often encountered in the untreated animal and vegetable oils used in leather manufacture but is likely to be present in tallow or other solid fat. The method given below is adapted to the determination of comparatively small percentages of water; for its determination in moellons, sulfonated oils, etc., see under the analysis of those materials.

Toluene Distillation Method (15).—Use the apparatus shown in Fig. 4 (Chap. II), and proceed as directed under determination of water in leather, using a sample of 100 g. of oil. Calculate and report percentage of

$$\text{Per cent H}_2\text{O} = \frac{\text{cc. water} \times 100}{\text{g. sample}}$$

ASH

The ash of untreated animal and vegetable oils should be negligible. If appreciable quantities are found, the ash should be analyzed as directed under sulfonated oils.

Weigh accurately about 10 g. into a weighed platinum dish. Heat gently over a small flame under a hood until the oil ignites, then supply only enough heat to maintain combustion until the sample is completely carbonized. Complete the ignition at dull red heat, preferably in an electric muffle, cool in a desiccator, and weigh. Calculate and report percentage of ash.

$$\text{Per cent ash} = \frac{\text{g. ash} \times 100}{\text{g. sample}}$$

SEDIMENT (MATTER INSOLUBLE IN BENZOL) (7)

The determination need not be made on liquid oils unless they are cloudy but should be made on solid fats.

Weigh accurately about 10 g. of fat into an ignited and weighed alundum thimble, and suspend it in a wide-mouth 500-cc. flask from a loop condenser, as shown in Fig. 79. Place about 100 cc. of benzol in the flask, taking care that the level of the liquid is below the bottom of the thimble. Heat to boiling on a hot plate, and regulate the heat so that the benzol condenses at a rate such that the thimble does not overflow. Extract for 1 hr.

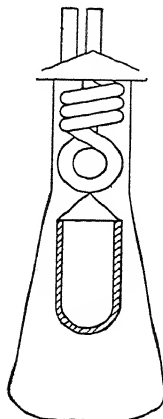


FIG. 79.—Apparatus for determining sediment in oils.

Remove the thimble, let the benzol drain out, dry in the air, and place in an oven at 105°C. for 1 hr. Cool in a desiccator, and weigh. Calculate percentage of sediment from the increase in weight of the thimble. If the percentage found is appreciable, ignite the thimble at dull red heat, cool in a desiccator, and weigh again. Calculate and report percentage of ash of sediment.

Per cent sediment =

$$\frac{\text{g. increase in weight after extraction} \times 100}{\text{g. sample}}$$

Per cent ash of sediment =

$$\frac{\text{g. increase in weight after ignition} \times 100}{\text{g. sample}}$$

UNSAAPONIFIABLE MATTER (8, 11, 23, 32, 34)

Unsaponifiable matter is determined by saponifying the fat with alcoholic sodium hydroxide and extracting the soap solution with petroleum ether.

Pure glycerides contain no unsaponifiable matter, since the fatty acids are converted into soap, and

the liberated glycerol is soluble in the aqueous soap solution. Natural fats, however, contain small quantities of materials that are not saponifiable, the amounts varying from mere traces up to several per cent depending upon the particular kind of fat. This unsaponifiable matter consists mostly of insoluble alcohols, such as cholesterol. Waxes, and some special fats such as wool grease, contain very large amounts of such substances. Mineral oils are not saponifiable, and the determination of unsaponifiable matter is a method for determining whether mineral oil has been added to animal and vegetable fats. In all cases where abnormal amounts of unsaponifiable matter are found, the material should be further examined, by determining its melting point and iodine number.

Weigh accurately about 3 g. of fat into a small flat-bottomed flask holding about 100 cc. Treat with 5 cc. of sodium hydroxide solution (500 g. per liter) and 45 cc. of alcohol. Close the flask with a cork pierced by a glass tube about 1 m. long and 6 to 8 mm. inside diameter, the lower end of which

projects about 1 cm. into the flask. This tube serves as a reflux condenser. Support the flask and tube on a hot plate, and boil for about 30 min. or until saponification is complete. Rinse the solution into a 1-l. separatory funnel with hot water. Place a 1,300-cc. casserole under the funnel to receive leakage. (The stopcock of the funnel must not be greased.) Cool the solution, add 100 cc. of petroleic ether (b. p. 40 to 60°C.), and rotate the funnel briskly, imparting a swirling motion to the contents, but do not shake, as the resulting emulsion may prove very difficult to break. Stopper loosely, and let the contents of the funnel stand overnight. Draw off all but about 1 cc. of the aqueous phase into a second funnel; it is necessary to leave a little water in the funnel to prevent loss of some of the ether layer. Reextract¹ the soap solution with fresh petroleum ether, draw off the soap solution, and add the petrol solution to that first obtained. Wash the combined petroleic ether solutions with successive small portions of water, drawing each off as soon as separation has taken place and uniting them with the main soap solution, until the washings no longer react alkaline to phenolphthalein. If emulsions form during the washing, they may be broken by adding a few drops of alcohol. Pour off the petroleic ether layer through a dry filter into a weighed glass crystallizing dish, taking care that the small amount of water left in the funnel does not accompany the ether solution. Rinse the funnel and paper 3 times with small quantities of petroleic ether, pouring each portion through the filter. Do not let the level of liquid in the dish rise within about 0.5 in. of the top, to avoid loss by creeping; if necessary, wait until part of the ether has evaporated before completing the washing. Finally, allow the petroleic ether to evaporate spontaneously in the air, place the dish in an oven at 100 to 105°C. for 30 min., cool in a desiccator for 15 min., and weigh. Calculate and report percentage of unsaponifiable matter.

$$\text{Per cent unsaponifiable matter} = \frac{\text{g. unsaponifiable matter} \times 100}{\text{g. sample weighed}}$$

If the percentage of unsaponifiable matter materially exceeds the normal value for the oil in question, determine its melting point and its iodine value as directed in this chapter. If necessary, repeat the determination, using a larger sample of oil to get enough material for these determinations.

Method of the A. L. C. A. for Unsaponifiable Matter in Hard Greases (6). Accurately weigh into a 300-ml. flask 5 g. of sample, add either 2.5 g. of potassium hydroxide dissolved in a little water or 5 ml. of a 50-per cent solution of potassium hydroxide and 25 ml. of 95-per cent alcohol. Boil with a reflux condenser for 1 hr. shaking occasionally. Glass beads may be used to prevent bumping. Add 50 ml. of hot water, cool, transfer to a separatory funnel, and extract 3 times, using 40 ml. of petroleum ether for each extraction. A little alcohol may be added to break persistent emulsions. Wash the combined petroleum ether solutions 3 times with a mixture of 30 ml. of water and 10 ml. of 95-per cent alcohol for each washing,

¹ When the amount of unsaponifiable matter is known to be small, a single extraction may suffice. Henrich, working in the authors' laboratory, found, in a commercial neat's-foot oil, 0.29 per cent unsaponifiable matter on one extraction and 0.47 per cent on three extractions.

transfer to a tared dish, evaporate to dryness, avoiding excessive drying, cool, and weigh. Calculate as percentage unsaponifiable.

UNOXIDIZED AND OXIDIZED FATTY ACIDS

On acidulating the soap solution obtained as described above, the fatty acids separate. These acids are classified as oxidized and unoxidized and can be separated by dissolving the latter in petrolic ether and then dissolving the former in alcohol. It is necessary first to remove alcohol from the soap solution. Care must be taken not to heat the soap in contact with the air, or oxidation of the unoxidized acids may occur.

Normal samples of most of the unaltered fats and oils used in leather making contain only small amounts of oxidized fatty acids. The chief reason for separating the unoxidized acids from these oils is in order to determine their melting point and iodine number, the first of which is directly important because high-melting fatty acids are likely to produce a spew, and the second because it is often more characteristic than the iodine value of the oil or fat itself. The determination of oxidized acids is of great importance in the analysis of moellons, vulcanized oils, and sulfonated oils.

Unoxidized Fatty Acids.—Boil the soap solution obtained as directed under determination of unsaponifiable matter in a casserole on the hot plate until all alcohol is removed. When this stage is reached, the solution generally ceases to froth. Wash down the sides of the casserole frequently with a stream of hot water, to prevent a ring of soap from being deposited; if this is not done, the soap may oxidize, and the value found for unoxidized acids will be too low. Transfer the solution quantitatively to a large separatory funnel, rinsing the casserole several times with hot water. Cool. Add a few drops of methyl orange or methyl red indicator. Treat the solution with dilute hydrochloric acid until distinctly acid; the fatty acids will then separate as a white cloud. Add 100 cc. of petrolic ether (b. p. 40 to 60°C.), and swirl the contents of the funnel. Stopper loosely, and let stand until the ether layer separates. Agitate again, let stand, and repeat until the water layer is entirely clear, except for such oxidized acids as may be present. The latter will generally be found floating in the interface as small brown particles, if present in small amounts; or as larger masses, sometimes sticking to the sides of the funnel, when their amount is larger. Draw off most of the water phase, through a filter (to retain oxidized acids), and wash the petrolic ether layer with successive portions of water until the washings no longer react acid to methyl red. Reject the washings and aqueous solution. Pour the petrolic ether solution through a dry filter into a weighed glass evaporating dish, and rinse the funnel and paper several times with small portions of the solvent, taking care not to fill the dish too full (see determination of unsaponifiable matter). Allow the ether to

evaporate, heat, cool in a desiccator, and weigh as directed under determination of unsaponifiable matter. Calculate and report percentage of unoxidized fatty acids. Determine melting point of the unoxidized fatty acids and their iodine number, as directed in this chapter.

Per cent unoxidized fatty acids

$$\frac{\text{g. unoxidized acids} \times 100}{\text{g. sample weighed for detn. of unsaponifiable}}$$

Oxidized Fatty Acids.—These will be found adhering to the walls of the funnel and on the two filters used for the water phase and the petrolic ether phase in separating the unoxidized acids.

Dissolve the oxidized acids in the funnel in hot alcohol, and pour the solution through the filter used for the petrolic ether solution, receiving the filtrate in a weighed glass dish. Rinse the funnel with hot alcohol, and wash the filter until it is colorless. Similarly, dissolve any oxidized acids which may be on the filter used for the water solution in the determination of unoxidized acids. When both filters and the funnel have been washed, evaporate most of the alcohol on the hot plate, but do not let the evaporation proceed to dryness. Allow the last of the alcohol to evaporate at room temperature. Heat at 100 to 105°C. for 30 min., cool in a desiccator, and weigh. Calculate and report percentage of oxidized fatty acids. Determine the iodine number of the oxidized acids, if the percentage found is appreciable, as directed in this chapter. The melting point of oxidized fatty acids is indefinite and of no significance.

Per cent oxidized fatty acids

$$\frac{\text{g. oxidized acids} \times 100}{\text{g. sample weighed for detn. of unsaponifiable matter}}$$

FREE FATTY ACIDS ("ACID NUMBER") (8), (23)

Free fatty acids are formed by hydrolysis of glycerides, which may be brought about by bacterial or enzyme action or by action of acids or alkalis. The free fatty acid content is therefore to some extent a measure of the deterioration which the fat has undergone. The percentage of free fatty acids normally present in commercial oils varies with the material.

Weigh accurately about 20 g., or less if the expected free acid content is high, into an Erlenmeyer flask. To 50 cc. of 95-per cent alcohol add a few drops of phenolphthalein, and titrate to a very faint pink with tenth-normal sodium hydroxide. Add this neutralized alcohol to the fat, and heat to boiling. Shake thoroughly. Titrate with tenth-normal sodium hydroxide until the pink color persists after vigorous shaking. Calculate and report percentage of free fatty acids as oleic acid or as acid number (= number of milligrams of potassium hydroxide required to neutralize the free fatty acids from 1 g. of fat).

$$\text{Per cent free fatty acid (as oleic)} = \frac{\text{cc. 0.1-N NaOH} \times 2.82}{\text{g. sample}}$$

$$\text{Acid number} = \frac{\text{cc. 0.1-N NaOH} \times 5.61}{\text{g. sample}}$$

Method of the A. L. C. A. for Free Fatty Acids in Hard Greases (6).—Dissolve 1 g. of sample in a mixture of 20 ml. of 95-per cent alcohol and 20 ml. of ethyl ether, which has been neutralized to phenolphthalein. Titrate the solution with tenth-normal sodium hydroxide, using phenolphthalein as indicator. Test for mineral acids or alkalis by adding methyl orange to a water emulsion of the sample, and if present make the necessary correction. Express the free fatty acids as percentage of oleic acid.

IODINE VALUE

Fats and oils that contain unsaturated fatty acids are capable of uniting with 2 atoms of iodine or other halogen at each double bond. The percentage by weight of iodine taken up by the fat is a measure of the unsaturation of the fatty acids it contains and is very characteristic. Solid fats, such as beef tallow, which consist mostly of glycerides of stearic and other saturated acids, have low iodine values; oils such as olive and neat's-foot, in which glycerides of oleic acid predominate, have iodine values in the neighborhood of 80; while highly unsaturated oils, such as linseed, cottonseed, and most marine oils, have iodine values that range well over 100.

The amount of halogen absorbed by a gram of oil varies with the conditions of the test, and hence great care must be taken to follow the prescribed procedure exactly. Several different methods, giving somewhat different results, have been proposed. Of these the Hanus method, employing a solution of iodine monobromide in glacial acetic acid, has been adopted as official by the Association of Official Agricultural Chemists (8), and is reproduced below. The Wijs method (4), employing a solution of iodine monochloride, has been adopted by the American Society for Testing Materials (7) for determining the iodine value of shellac. This method is given in Chap. XII.

Points to be observed are: The time of action of the halogen on the oil must be exactly 30 min.; the solution must be of the prescribed composition and strength; an excess of at least 60 per cent of the halogen taken must remain unabsorbed; a blank must always be run.

Hanus Iodine Solution (8).—Measure exactly 825 cc. of pure glacial acetic acid, and dissolve in it 13.615 g. of resublimed iodine with the aid of

heat. Add about 3 cc. of pure bromine to 200 cc. of glacial acetic acid. Measure exactly 25 cc. of the iodine solution, add 10 cc. of 15-per cent potassium iodide solution and 100 cc. of water, and titrate with tenth-normal sodium thiosulfate solution, adding the thiosulfate slowly, with shaking, until the color of the iodine solution fades to a light straw; then add a few drops of starch indicator, and continue the titration until the blue color is completely discharged. Measure exactly 5 cc. of the bromine solution, and titrate in the same way. Calculate the volume of bromine solution to add to the remaining 800 cc. of iodine solution in order exactly to double its halogen content.

Let

a = cc. Br. solution required

b = cc. $\text{Na}_2\text{S}_2\text{O}_3$ solution per cc. I solution

c = cc. $\text{Na}_2\text{S}_2\text{O}_3$ solution per cc. Br. solution

Then

800*b*

Add the calculated quantity of bromine solution to the iodine solution, dilute to exactly 1 l. with glacial acetic acid, and preserve the solution in a brown glass-stoppered bottle. Do not attempt to adjust the normality of the solution, but each time it is used determine its strength by means of a blank.

Hanus Procedure (8).—Weigh accurately about 0.25 to 0.5 g. (depending upon the iodine value expected) into a 500-cc., wide-mouth, glass-stoppered bottle. For oils, weigh several grams in a small beaker along with a small medicine dropper, transfer the approximate quantity of oil to the bottle, and reweigh. For solid materials, weigh the material in a dish or beaker without a pipette, scrape up approximately the desired weight on small, flattened pieces of glass rod, drop these rods into the bottle, and reweigh the dish.

Dissolve the oil or fat in exactly 10 cc. of chloroform. See that solution is complete before adding the iodine solution. Add from a burette exactly 25 cc. of Hanus iodine solution. Stopper, and let stand with occasional shaking for exactly 30 min.

If a number of determinations are to be run, add the iodine solution to the successive bottles at intervals of about 5 min., recording the time for each bottle. Similarly, run 2 blank determinations by adding 25 cc. of Hanus solution to 10 cc. of chloroform.

After 30 min. contact, add 10 cc. of a 15-per cent solution of potassium iodide, shake thoroughly, and then add 100 cc. of water. Titrate the excess iodine with approximately tenth-normal sodium thiosulfate solution, the "factor" of which has recently been determined as directed in Chap. XIII. Add the thiosulfate gradually, with constant shaking, until the yellow color of the iodine has almost disappeared. Then add a few drops of starch indicator, and continue the titration until the blue color disappears, shaking vigorously after each addition of thiosulfate.

Calculate the percentage of iodine absorbed by the oil, and report this value as the iodine value (Hanus method).

Let

= cc. $\text{Na}_2\text{S}_2\text{O}_3$ solution required for sample

B = cc. $\text{Na}_2\text{S}_2\text{O}_3$ solution required for blank

Then

$$\text{Iodine value} = \frac{(B - A) \times \text{Na}_2\text{S}_2\text{O}_3 \text{ factor} \times 1.27}{\text{g. sample}}$$

At least 60 per cent of the total halogen added must remain unabsorbed; i.e., A must be not less than $0.6B$. When more than two-fifths of the halogen added is absorbed, repeat the determination, using a smaller sample.

SAPONIFICATION (KOETTSCHDORFER) VALUE

The saponification value of a fat is the number of milligrams of potassium hydroxide required to saponify 1 g. of the fat. It is (in the absence of much unsaponifiable matter) a measure of the mean molecular weight of the fatty acids of the fat—the higher the molecular weight the lower the saponification number. A weighed sample of fat is treated with a measured excess of alcoholic potassium hydroxide solution until saponification is complete, and the excess determined by back-titration with standard acid, using phenolphthalein indicator. Care must be taken to see that the saponification is complete. With ordinary fats and oils this is easily accomplished by boiling for 30 min. with a half-normal solution of potassium hydroxide in 95-per cent alcohol, but for difficultly saponifiable substances, such as waxes, or materials containing much unsaponifiable matter, it is necessary to prepare the reagent with absolute alcohol and to add to the mixture an equal volume of benzol or of amyl alcohol (23).

Half-normal Alcoholic Potassium Hydroxide (8, 18).—Boil some 95-per cent ethyl alcohol under a reflux condenser with potassium hydroxide for several hours, distil off the alcohol, and to 1 l. of the distillate add 40 g. of the purest obtainable potassium hydroxide. Let stand until the insoluble carbonate has settled, decant the clear solution, and preserve in a well-stoppered bottle. Do not adjust the strength of the solution.

Determination (8).—Weigh accurately about 5 g. of fat into a small glass flask. Add from a pipette 50 cc. of the alcoholic potassium hydroxide solution, letting the pipette drain for a definite time. Measure a second 50-cc. portion of the reagent, under exactly the same conditions, into a second flask, to serve as a blank. Connect the flask with a reflux air-cooled condenser, and boil until saponification is complete (about 30 min.). Cool. Add a few drops of phenolphthalein indicator, and titrate the excess alkali with normal or half-normal hydrochloric acid till the color is discharged. Titrate the blank in the same way. The difference between the two titrations is a measure of the alkali consumed by the fat. Calculate the number of milligrams of potassium hydroxide absorbed by 1 g. of fat, and report the result as saponification value.

$$\text{Saponification value} = \frac{(B - A) \times 56.1}{\text{g. sample}}$$

B = cc. 1-N HCl consumed by blank

A = cc. 1-N HCl consumed by sample

HYDROXYL ("ACETYL") VALUE (8, 23)

When fatty acids that contain an alcoholic hydroxyl group are treated with acetic anhydride, the acetyl radical replaces the hydrogen of the hydroxyl group. When the acetylated fat is saponified with potassium hydroxide, the acetyl group forms an acetate. The hydroxyl, or "acetyl," value of a fat is the number of milligrams of potassium hydroxide required to neutralize the acetic acid liberated from 1 g. of acetylated fat.

Hydroxyl values of all the fats used in fat liquoring and stuffing (1) are quite low and not very characteristic, hence the determination is not useful for these materials. The determination of hydroxyl value is important in the case of castor oil (1) and in the case of waxes (23), which react with acetic anhydride by virtue of the hydroxyl groups of their higher alcohols.

Weigh accurately about 2 g. of fat into a small flask, treat with from 4 to 6 cc. of acetic anhydride, and boil under a reflux condenser for from 30 to 60 min. Immerse the flask up to the neck in hot water, stopper with a cork carrying 2 short glass tubes, extending a short distance into the flask, and pass a current of carbon dioxide, or other non-oxidizing gas, through the flask for 30 min. to remove the excess of acetic anhydride. Add 25 cc. of ether and 5 cc. of water, and neutralize the last traces of anhydride with tenth-normal sodium hydroxide. Add from a pipette 50 cc. of alcoholic half-normal potassium hydroxide, and saponify exactly as described under determination of saponification value. Titrate the excess alkali with normal or half-normal hydrochloric acid, using phenolphthalein indicator.

Saponify about 4 g. of non-acetylated fat with 50 cc. of half-normal alcoholic potassium hydroxide, and conduct a blank on the potassium hydroxide solution, as described under determination of saponification value. Titrate the excess potassium hydroxide with standard acid.

Calculate hydroxyl value as follows:

Let

a = cc. 1-N HCl for back-titration of acetylated fat

b = cc. 1-N HCl for back-titration of saponified fat

c = cc. 1-N HCl for back-titration of blank

Then

$$\text{Hydroxyl value} = \frac{(c - a)}{\text{g. fat}} - \frac{(c - b)}{\text{g. fat}} \times 56.1$$

acetylated saponified

MAUMENÉ ("THERMAL") VALUE (23)

When animal or vegetable fats are treated with strong sulfuric acid, the acid combines with the oil, forming a sulfonated oil and liberating much heat. The rise in temperature produced when a given sample of oil is treated with a given quantity of acid is called the Maumené value. The quantity of heat liberated increases with increasing degree of unsaturation of the fat, and Maumené values therefore run roughly parallel to iodine values. Maumené values are less reproducible than are iodine values, and the determination has been dropped from many official procedures.

Weigh exactly 50 g. of oil into a 150-cc. beaker. Bring the oil and the sulfuric acid to be used to exactly the same temperature. Surround the oil beaker with a thermal insulator; a short section of steam pipe cover is very convenient. Measure with a pipette exactly 10 cc. of concentrated (sp. gr. 1.84) sulfuric acid, and run the acid into the oil, stirring the mixture continuously with a thermometer. After the acid is all in, continue to stir the mixture, observing the temperature every few seconds, until the temperature reaches a maximum and begins to fall. Record the highest temperature attained. Take the difference between the initial and the maximum temperatures as the Maumené value.

In the case of cottonseed oil, cod oil, and other oils having very high Maumené values, the sample must be diluted with an inert oil before making the test. Determine the Maumené value of a mineral oil as directed above. Weigh 25 g. of the oil to be examined and 25 g. of the mineral oil, mix, and determine Maumené value of the mixture. Multiply the observed rise in temperature by 2, and subtract the Maumené value of the diluent to obtain the Maumené value of the oil under examination.

ANALYSIS OF MINERAL OIL AND PARAFFIN

Mineral oil is sometimes used in fat liquoring skin in conjunction with other materials, particularly sulfonated oils. It is often used for "oiling off" leather that has already been fat liquored, either alone or in combination with such oils as olive, cottonseed, castor, etc. Paraffin is used in stuffing heavy leathers.

The same tests that are used on the true fats and oils may also be applied to mineral oils, but the relative importance of the tests is somewhat different. Mineral oil should consist almost entirely of unsaponifiable matter. The iodine value, Maumené value, and saponification value should be very low. No unoxidized or oxidized fatty acids should be present. The physical constants of the oil generally will be found sufficient to charac-

terize a given sample and to ensure a constancy of composition from one shipment to another. The authors determine specific gravity, viscosity, cloud point, Maumené value, and free mineral acid (or alkali) in the routine examination of successive shipments of mineral oil from the same source.

Viscosity, cloud point, and gravity show whether or not different samples have the same physical properties, Maumené value is a rapid and simple method of detecting possible admixture of animal or vegetable oil, and the determination of free acid guards against possible damage to the leather from acid left in the oil from the refining process. In examining a sample from an untried source, the material is analyzed completely by the methods given in the preceding section.

The most important single characteristic of paraffin wax is its melting point. The "American Society for Testing Materials paraffin wax melting point" is defined (7) as "the temperature at which melted paraffin wax, when allowed to cool under definite prescribed conditions, first shows a minimum rate of cooling." The so-called "American melting point" is an arbitrary figure 3°F. higher than the A. S. T. M. paraffin wax melting point.

Melting Point of Paraffin Wax (Based on Standard Method D87-22, A. S. T. M.) (7).—Arrange an apparatus as shown in Fig. 80. A test tube measuring 1 by 4 in. is supported in an air bath measuring 2 by 4½ in., which in turn is supported in a water bath. The water bath is provided with a thermometer accurate to 2°F. The test tube is stoppered with a cork carrying a sensitive thermometer and pierced with a hole for a wire stirrer. The thermometer prescribed by the A. S. T. M. covers a range of 27 to 71°C. in 0.1°C. subdivisions, must be accurate to 0.1°C. throughout the scale, is sealed for 79-mm. immersion, and measures 105 to 115 mm. from the bottom of the bulb to the 27°C.-line and 25 to 40 mm. from the 71°C.-line to the top of the thermometer.

Melt the paraffin in a water bath (not over a free flame or on a hot plate) at a temperature not more than 35°F. above the approximate melting point. Fill the tube with melted wax to a height of 2 in. Insert the cork into the tube for ½ in., with the 79-mm. immersion line of the thermometer at the

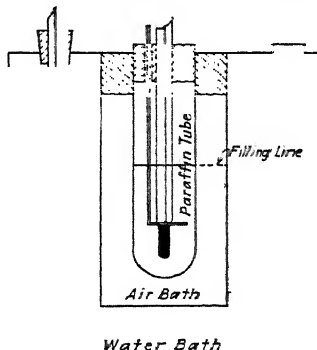


FIG. 80.—Apparatus for determining melting point of paraffin wax.

under surface of the cork. The lower end of the thermometer will then be $\frac{3}{8}$ in. from the bottom of the tube. Fill the water bath with water at a temperature 15 to 20°F. below the expected melting point. Insert the wax tube into the air bath in a central vertical position so that the bottom is $\frac{1}{2}$ in. above the bottom of the air bath and the sides $\frac{1}{2}$ in. distant from the walls of the air bath. Let the wax cool to a temperature 10°F. above its expected melting point. Adjust the temperature of the water bath so that it is then from 25 to 35°F. below that of the wax. Do not further stir or adjust the water bath. Stir the wax by moving the wire loop up and down through the entire length of the test tube in a steady motion at the rate of 20 cycles per minute. Read the melting point thermometer to the nearest 0.1°F. every 30 sec., and record the readings. The temperature of the wax will fall gradually at first, will then become almost constant, and will then again fall gradually. Continue making and recording readings every 30 sec. for 3 min. after the temperature again begins to fall. Inspect the recorded readings, and take the average of the first 4 readings that lie within 0.2°F. as the uncorrected melting point. Correct if necessary for any error in the thermometric scale, and report the results as the "A. S. T. M. paraffin wax melting point." Duplicate determinations should differ by not more than 0.2°F.

ANALYSIS OF MOELLON DÉGRAS (6, 20, 23, 37, 45, 51)

Moellon *dégras* is a by-product of the oil tannage of sheepskins in the manufacture of chamois leather (54). Oil tannage is carried out by pummeling the skins with various unsaturated and easily oxidized oils, particularly cod oil and other oils of marine origin. Heat is evolved, the oils become oxidized, and part of the oil is fixed by the skin. The excess oil is pressed out after saturating the skins with water and constitutes the purest and best grade of moellon *dégras*. An inferior grade is obtained by washing the oil-tanned skins with water and sodium carbonate, neutralizing the resulting emulsion, and salting out the liberated oil. Gnamm (23) states that the product so obtained is often mixed with the pure moellon previously expressed. He states further that as the supply of moellon is inadequate to meet the demand, the oil-tanning process is sometimes carried out with the direct purpose of manufacturing moellon, the skins being pummeled again and again with fresh portions of oil until they are worn out. With each treatment and pressing the quality of the moellon produced becomes lower. Animal and vegetable oils are sometimes added to natural moellon. Finally there are on the market various artificial moellons or moellon substitutes, some of which contain blown oils and hence contain the oxidized fatty acids characteristic of moellon, while others are mere mixtures of wool grease with other oils (23).

Moellon *dégras* is a dark-colored, viscous emulsion, usually containing about 25 per cent water. The characteristic constituent of moellon is its oxidized fatty acids, sometimes known as "*dégras formers*." The percentage present is quite variable, ranging from about 7 to nearly 20 per cent in some samples examined by the authors, but averages about 10 per cent. The free fatty acid content of moellon is generally high. In normal specimens the unsaponifiable matter present is low, but sometimes samples are met with that contain very large percentages of unsaponifiables, derived from wool grease. Moellon should contain less than 1 per cent ash and be free from mineral acid. The average composition of samples of pure, natural moellon examined by the authors during the past 10 years is given in Table 52 (54).

TABLE 52.—AVERAGE COMPOSITION OF NATURAL MOELLON

Constituent:	Per cent
Water.....	25.25
Unsaponifiable matter.....	1.71
Unoxidized fatty acids.....	51.91
Iodine value.....	80
Melting point, degrees Centigrade.....	28
Oxidized fatty acids.....	10.44
Iodine value.....	83
Ash.....	0.82
Free fatty acids (as oleic acid).....	15.66
Free mineral acid.....	0.00

The A. L. C. A. methods (6) provide for the determination of water, ash, unsaponifiable matter, oxidized fatty acids, and free acids. The authors determine, in addition, unoxidized fatty acids and determine iodine value and melting point of the unoxidized and iodine value of the oxidized acids.

WATER

Water is determined by heating a weighed sample in a platinum dish over a small free flame until all moisture is expelled. When this point is reached, moisture will no longer gather on a cold watch glass held over the dish, and the surface of the oil gives off little wreaths of smoke, accompanied by a slight crackling sound. With practice, duplicate results can be obtained consistently that differ by less than 0.5 per cent.

A. L. C. A. Method (6).—Accurately weigh 3 g. of sample into a wide platinum dish, and heat with a low flame until all moisture is driven off. This point can be determined by the appearance of smoke and a slight crackling sound. Place the dish in a desiccator, cool, and weigh.

ASH

A. L. C. A. Method (6).—Ash the residue from the moisture determination at dull red heat, cool, and weigh.

UNSAAPONIFIABLE MATTER

Determine as directed under analysis of fats and oils, (this chapter).

UNOXIDIZED FATTY ACIDS

Determine percentage of unoxidized fatty acids and their iodine value and melting point, as directed under analysis of fats and oils (this chapter).

OXIDIZED FATTY ACIDS

Determine as directed under analysis of fats and oils, or by the A. L. C. A. method below. The latter differs from the authors' procedure only in that the unoxidized acids are not saved and weighed.

A. L. C. A. Method (6).—Boil the soap solution remaining from the unsaponifiable determination until all the alcohol is expelled. Dissolve in hot water, and transfer to a separatory funnel, rinsing the beaker thoroughly and bringing the volume to about 300 ml. Immediately add an excess of concentrated hydrochloric acid, about 25 per cent more than sufficient to neutralize the total alkali, rotate the flask vigorously, cool, and shake out with petroleum ether. Run off the aqueous layer, and pour off the ether layer, avoiding loss of oxidized fatty acids. Wash the acids twice with a small quantity of petroleum ether and twice with a small quantity of hot water, dissolve them in warm 95-per cent alcohol, filter if necessary, transfer to a tared dish, place in the evaporator and dryer for 16 hr., cool, and weigh. Conduct the entire determination without delay.

MINERAL ACID

Weigh accurately about 10 g. of moellon, shake with 50 cc. of water in a small flask, and test the aqueous layer with methyl orange. If mineral acid is present, as shown by the production of a red color, titrate with tenth-normal sodium hydroxide to the neutral point. Calculate and report as percentage of sulfuric acid.

FREE FATTY ACID

Determine as directed under analysis of fats and oils or by the A. L. C. A. method for free fatty acid in hard greases (6), which is also official for moellon.

ANALYSIS OF SULFONATED OILS (6, 13, 21, 23 to 28, 50 to 52)

Sulfonated oils are made (54) by treating animal or vegetable oils with strong sulfuric acid. The sulfuric acid combines with

the fatty acids of the oil (the exact position at which it enters the molecule is in dispute), forming a sulfo-fatty acid of the general formula $R-SO_3H$, where R is a fatty acid radical. Thus castor oil, containing ricinoleic acid, forms sulforicinoleic acid. On treatment with ammonia or fixed alkali, sulfo-fatty acids form salts, for example sodium sulforicinoleate. The amount of sulfuric acid that enters into combination with the oil varies with the ratio of acid to oil, the time, and the temperature. Sulfonation is never carried to completion, but conditions are so regulated as to produce a product of a degree of sulfonation that has been found to give a product of the desired properties.

After sulfonation is complete, the oil-acid mixture is washed with strong sodium sulfate solution, whereupon the sulfonated oil separates as an oily layer, and the excess acid is dissolved in the brine. After separation of the oil layer from the brine, the sulfo-fatty acids are neutralized with fixed alkali or with ammonia. The principal sulfonated oils used in fat liquoring are sulfonated neat's-foot and sulfonated cod. Sulfonated castor oil is used in oiling off. Sulfonated oils are used also for stabilizing the ground mineral pigments used in water finishes.

Sulfonated oils behave with water very much like soaps, forming solutions or emulsions that are almost optically clear and that, unlike soap solutions, are stable over a considerable range of pH value. The sulfonated oil is separated from such a solution by salting out. In contact with leather, a solution of a sulfonated oil gives up oil to the leather. Sulfonated oil is also capable of acting as an emulsifying agent for neutral fatty oils or for mineral oil. This fact, as well as its own fat liquoring properties, causes sulfonated oil to be used very widely in fat liquoring light leathers.

The sulfonated oils of commerce are viscous, semitransparent liquids, varying in color from light yellow to dark brown, depending upon the kind of oil employed. The oil contains a variable amount of water, usually in the neighborhood of either 50 or 25 per cent. Usually, a little sodium sulfate is present, and sometimes free acid or free alkali. The analysis of the oil includes the determination of these impurities, the nature of the oil itself, the extent of sulfonation, the nature of the neutralizing agent, and the amount of neutral fatty oil or mineral oil that may have been added. Frequently, sulfonated oils are mixed with neutral oils, diluted, and sold as "fat-liquor oils." The analysis

of such fat-liquor oils is carried out exactly like that of pure sulfonated oils.

The average composition of samples of sulfonated neat's-foot (two types), cod, and castor oil analyzed in the authors' laboratories during the past 10 years is shown in Table 53 (54).

TABLE 53.—COMPOSITION OF TYPICAL SULFONATED OILS USED IN FAT LIQUORING

Constituent	Sulfonated oil			
	Neat's-foot		Cod liver	Castor
	(1)	(2)		
Specific gravity at 15.5°C.....	0.990		0.990	1.046
Water, per cent.....	22.05	52.67	18.22	59.80
Unsaponifiable matter, per cent.....	0.10	0.25	0.02	0.10
Unoxidized fatty acids, per cent.....	54.35	36.78	51.85	19.01
Iodine value.....	70	70	82	66
Melting point, degree centigrade.....	30	32	27	14
Oxidized fatty acids, per cent.....	0.18	1.07	19.11	4.04
Total sulfates (as sulfur trioxide), per cent.....	4.26	0.92	4.30	3.14
Sulfur trioxide combined with oil, per cent.....	3.50	0.89	3.45	2.55
As sulforicinoic acid, per cent.....	16.54	4.20	16.30	12.06
Total fatty oil, per cent.....	72.98	44.80	77.89	32.36
Ammonia, per cent.....	0.00	0.00	0.19	0.00
Ash, per cent.....	4.87	2.28	3.87	7.74
Sodium sulfate, per cent.....	4.87	0.73	3.65	5.50
Sodium chloride, per cent.....	0.00	0.19	0.00	0.59
Sodium carbonate, per cent.....	0.00	1.22	0.00	1.65

WATER

Determine as directed for moellon *dégras* or by the toluene distillation method, prescribed by the A. L. C. A. (6) and given below.

A. L. C. A. Method. *Apparatus.*—Assemble the apparatus as illustrated in the *Journal of the American Leather Chemists Association*¹ (see Fig. 4), using a 500-ml. Erlenmeyer or distilling flask, a sealed-in, straight tube, Liebig condenser about 10 in. long, with a delivery end approximately 3/8 in. in diameter, and a special collecting tube graduated in tenths of a milliliter.

¹ 21, 387, 1926.

Before each distillation clean the condenser and receiving tube with chromic-sulfuric acid mixture, rinse thoroughly with water, then with alcohol, and dry either in an oven or with a current of air. Calibrate the receiving tube or check its graduation by distilling toluene containing known quantities of water. Read the bottom of the meniscus of the water column and estimate as closely as possible to hundredths of a milliliter.

Toluene.—Use dry toluene having a boiling point under normal pressure of 110 to 112°C.

Determination.—Weigh into the distilling flask a quantity of sample that contains preferably between 3 and 5 ml. of water. Immediately add about 100 ml. of toluene, and connect the flask with the receiving tube and condenser. Fill the receiving tube with toluene, pouring it through the condenser. Heat gently, and distill at the rate of about 4 drops per second for 2 hr. At the end of 1, 1¼, 1½, 1¾, and 2 hr. distillation wash down the condenser by pouring in at the top of it a small quantity of toluene while brushing thoroughly with a tight-haired, close-fitting tube brush that has been boiled previously in toluene. At the end of 2 hr. disconnect the receiving tube, dislodge any drops of water on the inside of it by rubbing with a piece of light copper wire twisted at one end into a loop, and let the tube come to laboratory temperature. Read the volume of water to 0.01 ml., and make such calibration correction as may be necessary. Assume that 1 ml. of water weighs 1 g., and calculate the percentage of moisture.

ASH

Ash may be determined in the sample used for determining water, if the free flame method for water is employed, or in a separate sample, according to the method of the A. L. C. A. (6).

A. L. C. A. Method.—Weigh accurately from 5 to 10 g. of sample into a crucible or dish, ignite gently, allowing the oil to burn, and then complete the incineration at a dull red heat until all the carbon is burned off. Cool and weigh.

UNSAAPONIFIABLE MATTER, UNOXIDIZED, AND OXIDIZED FATTY ACIDS

Unsaaponifiable matter, unoxidized fatty acids, and oxidized fatty acids are determined much like the corresponding constituents of a neutral fatty oil. According to Stiasny (50), it is necessary first to decompose the sulfo-fatty acids by boiling the oil with dilute hydrochloric acid. The total fatty matter is then separated from the aqueous solution by extraction with ether, the ether is evaporated, and unsaaponifiable matter, unoxidized, and oxidized fatty acids determined in the residue in the usual way. Henrich, working in the authors' laboratory, found the same percentages for oxidized and unoxidized fatty acids, whether the sample was decomposed with acid or saponified directly.

The A. L. C. A. methods provide for the determination of unsaponifiable matter only.

Authors' Method.—Weigh accurately about 3 g. of oil into a small flask. Treat the sample with alcohol and strong potassium hydroxide, and determine unsaponifiable matter, unoxidized fatty acids, and oxidized fatty acids, as described under analysis of fats and oils. Determine iodine value and melting point of the unoxidized fatty acids and of the unsaponifiable matter and oxidized fatty acids if enough of either of these constituents is present, as previously described.

A. L. C. A. Method for Unsaponifiable Matter (6).—Weigh accurately about 10 g. of sample into a 250-ml. flask, add 50 ml. of an alcoholic solution of potassium hydroxide approximately normal, boil 1 hr. under a reflux condenser, and cool. Add 40 ml. of water, and transfer to a separatory funnel. Shake out at least 3 times with petroleum ether, boiling between 40 to 75°C., using 50 ml. each time. Wash the combined petroleum ether extracts at least 3 times, using a slightly alkaline 50-per cent solution of alcohol the first time and water subsequently. Evaporate the petroleum ether extract in a tared dish, dry, cool, and weigh.

TOTAL ALKALI

Total alkali is determined by titration of the aqueous solution of the oil, using methyl orange indicator.

A. L. C. A. Method (6).—Weigh 10 g. of sample into a 250-ml. flask, dissolve in 150 ml. of water, warming to obtain solution if necessary. Add 30 g. of granulated sodium chloride, 25 ml. of ether, and 5 ml. of methyl orange indicator (0.1-per cent solution), and titrate with half-normal sulfuric acid. Calculate to milligrams of potassium hydroxide per gram of sample. Let this value equal *A*.

Authors' Method.—Proceed exactly as above, but calculate percentage of total alkalinity as sodium oxide, Na_2O .

$$\text{Per cent total alkali as Na}_2\text{O} = \frac{\text{cc. 0.5-N H}_2\text{SO}_4 \times 1.55}{\text{g. sample}}$$

COMBINED AND FREE FATTY ACIDS

A. L. C. A. Method (6).—Weigh 8 g. of sample into a 500-ml. beaker. Add 50 ml. of 95-per cent alcohol and several drops of phenolphthalein solution. Titrate with half-normal sodium hydroxide until the end point is reached, boil gently until no more ammonia is given off as shown by testing with moistened red litmus paper, cool, add half-normal sodium hydroxide again until the pink color persists, boil to drive off any remaining ammonia, cool, and titrate to the end point with half-normal sodium hydroxide. Record the total number of milliliters of half-normal sodium hydroxide required for the titration. Add 150 ml. of water and 5 ml. of methyl orange indicator, and titrate to the acid end point with half-normal acid. The number of milliliters of half-normal sulfuric acid required corresponds to

the combined and free fatty acids. Calculate to milligrams of potassium hydroxide per gram of sample, and let this value equal *B* or the combined and free fatty acids expressed as milligrams of potassium hydroxide per gram.

The [content of] free fatty acids, expressed as milligrams of potassium hydroxide per gram of sample, is the difference between *B*, obtained under Combined and Free Fatty Acids, and *A*, obtained under Total Alkali, or $B - A$.

AMMONIA (35, 53)

Ammonia may be calculated from the data obtained in the determination of combined and free fatty acids by the A. L. C. A. methods, or directly by distillation.

A. L. C. A. Method (6).—The number of milliliters of half-normal sulfuric acid minus the number of milliliters of half-normal sodium hydroxide required for the respective titrations under Combined and Free Fatty Acids corresponds to the alkali minus ammonia, NH_3 . This value in the presence of ammonium salts may be a minus quantity. Preserve the sign, calculate to milligrams of potassium hydroxide per gram of sample, and let this value equal *C*. Then the percentage of ammonia, NH_3 , equals *A*, obtained under Total Alkali, minus *C* multiplied by 1.703 and divided by 56.1, or

$$\frac{(A - C) 1.703}{56.1}$$

Distillation Method.—Place several grams of oil in a test tube, dilute with water, add about 1 cc. of strong sodium hydroxide solution, and warm gently. Test for ammonia by odor and by holding a piece of moist red litmus paper in the mouth of the tube. If ammonia is found to be present, weigh accurately about 10 g. of oil into a Kjeldahl flask, add about 200 cc. of water and about 100 cc. of butanol, and connect the flask to a condenser by means of a distilling head, as described in Chap. II. Place 50 cc. of tenth-normal sulfuric acid in a receiving flask, and connect the receiver to the outlet of the condenser. Add about 5 cc. of strong sodium hydroxide solution to the contents of the flask, by means of the funnel shown in Fig. 5. Heat to boiling, and distill until at least 100 cc. of water has collected in the receiver. The butanol forms a layer over the aqueous solution in the flask and prevents frothing. Part of the butanol is steam distilled and collects in the receiver above the acid solution. If the butanol in the flask is nearly all distilled, add more through the funnel. When distillation is complete, disconnect the receiver and titrate the excess acid with tenth-normal sodium hydroxide, using methyl red indicator. Calculate and report percentage of ammonia.

$$\text{Per cent NH}_3 = \frac{(50 - \text{cc. 0.1-N NaOH}) \times 0.17}{\text{g. sample}}$$

TOTAL SULFATE, SULFATE COMBINED WITH OIL, AND SODIUM SULFATE

The commonest method for determining sulfate combined with oil is to determine total sulfate gravimetrically and uncombined sulfate in a solution obtained by extracting the oil either with strong sodium chloride solution or with monosodium phosphate solution (33). Sulfate combined with oil is obtained by difference. By the A. L. C. A. method, the sulfate combined with the oil is liberated by boiling with a measured quantity of standard acid. The liberated sulfuric acid is titrated, deducting, of course, the quantity of alkali required to neutralize the sulfuric acid added to decompose the sulfo-acid. Combined sulfate is calculated from the net quantity of alkali required to neutralize the liberated acid, plus the quantity of alkali originally present in the oil, as found in the determination of total alkali.

Gravimetric Method for Total Sulfate.—Weigh accurately about 2 g. of oil into a platinum dish. Add about 20 g. of pure, anhydrous sodium carbonate, and mix thoroughly with a stiff platinum wire. Brush off any of the mixture adhering to the wire. Add a layer of pure sodium carbonate about $\frac{1}{8}$ in. thick. Heat the dish gently in an electric muffle furnace until the oil ignites, then continue the ignition at dull red heat until most of the carbon is consumed. Cool. Dissolve the contents of the dish in water, filter, and wash the paper free from sulfates. Acidify with hydrochloric acid, add bromine water until the solution remains colored, heat to boiling, and boil until the excess bromine is expelled. To the hot solution add about 10 cc. of a 10-per cent solution of barium chloride, drop by drop. Let the precipitate settle for several hours, filter through Whatman No. 44 paper or its equivalent, and wash free from chlorides. Dry the paper, ignite in a weighed crucible, beginning at a low temperature, gradually raising the temperature to the maximum attainable with an ordinary burner, and allowing free access of air to the contents of the crucible. Cool in a desiccator, and weigh as barium sulfate. Calculate percentage of total sulfate as sulfur trioxide.

$$\text{Per cent SO}_3 = \frac{\text{g. BaSO}_4}{\text{g. sample}}$$

Uncombined Sulfate (Kern's Method) (33).—Weigh accurately about 40 g. of oil into a small separatory funnel, and treat with exactly 100 cc. of approximately 15-per cent monosodium phosphate solution. Shake vigorously several times. Let stand until the oily layer separates (overnight). Draw off as much as possible of the aqueous phase, which contains all the sulfate not combined with the oil, through a dry filter paper into a dry receiver. Pipette exactly 50 cc. of the filtrate into a beaker, dilute to about 200 cc., add 10 cc. of concentrated hydrochloric acid, and precipitate and weigh barium sulfate as directed above. Calculate and report percentage

of sulfate not combined with the oil, taking into account the water in the sample weighed.

$$\text{Per cent uncombined SO}_2 = \frac{\text{g. BaSO}_4 \times 34.3 \times 100}{\text{g. sample} \times 50} + A$$

where $A = \text{g. H}_2\text{O in sample weighed}$

Alternate Method for Uncombined Sulfate.—Weigh accurately about 40 g. of oil into a small separatory funnel, and shake with 10 cc. of saturated sodium chloride solution. After the oily layer separates, draw off as much as possible of the aqueous phase into a beaker, and treat the oil with a fresh 10-cc. portion of salt solution. Repeat until the last solution drawn off gives only a faint test for sulfate with barium chloride. Combine the salt solutions, acidify the solution with hydrochloric acid, and precipitate and weigh barium sulfate in the usual way.

NOTE.—The above method is that given in most texts. The authors have found Kern's method to give the same results and to be considerably less time consuming.

Combined Sulfate.—Subtract percentage of uncombined sulfate from percentage of total sulfate, both determined as above, and report the difference as percentage of sulfate combined with the oil as sulfur trioxide. Multiply the result by the factor 4.725, and report the product as percentage of sulfate combined with the oil as sulforicinoleic acid.

Per cent combined $\text{SO}_2 = \text{per cent total SO}_2 - \text{per cent uncombined SO}_2$
 Per cent combined sulfate as sulforicinoleic acid =

$$\text{per cent combined SO}_2 \times 4.725$$

A. L. C. A. Method for Combined Sulfur Trioxide.—Weigh 8 g. of sample into a 300-ml. flask, and boil for 1 hr. under a reflux condenser with 25 ml. of normal sulfuric acid, using glass beads to prevent bumping. Shake frequently. Rinse the condenser, disconnect the flask, and cool. Add about 30 ml. of ether, 100 ml. of water, 30 g. of granulated sodium chloride, and 5 ml. of methyl orange indicator. Titrate with half-normal sodium hydroxide. Frequently stopper and shake the flask during the titration. Deduct the equivalent of the added sulfuric acid from the quantity of sodium hydroxide required for the titration, and calculate the difference to milligrams of potassium hydroxide per gram of sample. Let this value equal F . Then the percentage of combined sulfur trioxide equals the sum of F plus A , obtained under Total Alkali, multiplied by 8 and divided by 56.1, or

$$\frac{(F + A)}{56.1} \times 8$$

A. L. C. A. Method for Neutralized Combined Sulfur Trioxide.—The percentage of neutralized combined sulfur trioxide equals $1.49 \times$ percentage of combined sulfur trioxide).

A. L. C. A. Method for Sodium Combined as Soap.—The percentage of sodium combined as soap equals $0.041C$. The value for C is obtained under Ammonia.

ANALYSIS OF ASH

The constituents ordinarily determined are sodium sulfate and sodium carbonate. These may be determined directly by the usual methods or calculated according to the methods of the A. L. C. A. given below (6).

Direct Methods.—To the ash, obtained as described above, add 10 cc. of tenth-normal hydrochloric acid. Let stand for a few minutes, add a few drops of methyl orange indicator, and add more acid in case the solution is alkaline. Rinse the solution into a beaker, and titrate the excess hydrochloric acid with tenth-normal sodium hydroxide. Calculate and report percentage of sodium carbonate. Filter the solution, wash the filter paper free from chlorides, and determine sulfate in the filtrate in the usual way. Calculate and report percentage of sodium sulfate.

$$\text{Per cent Na}_2\text{CO}_3 \text{ in ash} = \frac{(A - B) \times 0.53}{\text{g. sample weighed for ashing}}$$

where A = cc. 0.1- N HCl
and B = cc. 0.1- N NaOH

$$\text{Per cent } \text{BaSO}_4 \text{ in ash} = \frac{\text{g. BaSO}_4 \times 60.86}{\text{g. sample weighed for ashing}}$$

A. L. C. A. Method. Sodium Sulfate, Na_2SO_4 , in the Ash.—The percentage of sodium sulfate, Na_2SO_4 , in the ash from combined sulfur trioxide equals $0.1268 [C + (F + A)]$. When $C > (F + A)$, substitute $(F + A)$ for C . The value for A is obtained under Total Alkali, that for C under Ammonia, and that for F under Combined Sulfur Trioxide.

Sodium Carbonate, Na_2CO_3 , in the Ash.—The percentage of sodium carbonate, Na_2CO_3 , in the ash due to fixed alkali combined as soap equals $0.0946 [C - (F + A)]$. When the term $[C - (F + A)]$ is negative, there can be no carbonate in the ash. The value for A is obtained under Total Alkali, that for C under Ammonia, and that for F under Combined Sulfur Trioxide.

Total Salts and Impurities.—The percentage of total salts and impurities in the oil equals the ash — sodium sulfate — sodium carbonate.

TOTAL AND NEUTRAL FATTY MATTER

Total fatty matter is taken as the difference between the sum of the non-fatty constituents and 100. If the methods of the A. L. C. A. are used throughout, the total fatty matter should be calculated by the A. L. C. A. method given below. The authors add percentages of water, ash, unsaponifiable matter, and ammonia and subtract the sum from 100. By this method, non-neutralized sulfate combined with the oil would be included as fatty matter.

A. L. C. A. Method for Total Fatty Matter (6).—The difference between 100 and the sum of moisture, unsaponifiable, ammonia, sodium as soap, neutralized combined sulfur trioxide, and total salts and impurities in the oil is the percentage of total fatty matter.

A. L. C. A. Method for Neutral Fatty Matter (6).—Calculate the value *B* as obtained under Combined and Free Fatty Acids to percentage of oleic acid, and subtract the result from the percentage of total fatty matter. The difference equals the percentage of neutral fatty matter.

SEPARATION OF SULFONATED AND UNSULFONATED OIL

Methods of investigating sulfonated oils, that have not come into general use as control methods, but which appear to be very useful in studying the constitution of such oils, have been devised by Stiasny and Riess (50), and by Schindler and Schacherl (55). According to Stiasny and Riess, sulfonated oils may be divided into three fractions: *A*, soluble in 80-per cent alcohol but insoluble in petroleum ether; *B*, soluble both in alcohol and petroleum ether; and *C*, soluble in petroleum ether but insoluble in alcohol. Fraction *A* is most highly sulfonated, fraction *B* lightly sulfonated, and fraction *C* practically free from sulfate. With increasing degree of sulfonation, fraction *C* decreases to a minimum, fraction *A* + fraction *B* increases to a maximum, and the ratio of *A* to *B* increases.

Stiasny-Riess Method (50).—Weigh accurately about 3 g. of oil, and dissolve in about 50 cc. of ethyl ether in a separatory funnel. Add an equal volume of 10-per cent sodium chloride solution, and shake thoroughly. Add a few drops of methyl orange indicator, and titrate with dilute sulfuric acid until the solution is just acid, shaking after each addition of acid. Draw off the water layer, and wash the ether layer with small portions of the salt solution until the last portion gives no test for sulfates. Transfer the ether solution to a small flask, evaporate the ether on the water bath, and treat the residue with about 50 cc. of 80-per cent alcohol. Return the solution to the separatory funnel, and rinse the flask three times with 80-per cent alcohol and then three times with petroleum ether, adding the rinsings to the solution in the funnel. Then add petroleum ether to the funnel until it is present in volume approximately equal to that of the alcohol. Shake thoroughly, let stand until the phases separate, and draw off the alcohol layer into a second funnel. Shake the alcohol solution again with petroleum ether, and draw off the alcohol solution into a third funnel. Shake the solution a third time with petroleum ether, and then draw off the alcohol solution into a weighed evaporating dish, evaporate to dryness, dry the residue in an oven at 105°C. for 15 min., and weigh. The residue represents fraction *A* (soluble in alcohol, insoluble in petroleum ether).

Combine the petroleum ether solutions obtained above, and shake out the petroleum ether solution three times with fresh portions of 80-per cent alcohol, drawing off each portion in turn into the same weighed dish. Evaporate and weigh the residue, which consists of fraction *B* (soluble both in alcohol and in petroleum ether).

Draw off the petroleum ether solution into a weighed dish, evaporate, and weigh. The residue represents fraction *C* (soluble in petroleum ether, insoluble in alcohol).

Calculate and report percentages of fractions *A*, *B*, and *C* in the oil.

Schindler-Schacherl Method.—Weigh 5 g. of sulfonated oil (containing 70 per cent of fat) into a small separatory funnel and shake vigorously with 25 cc. of 96-per cent alcohol. Let stand 30 min., shake again, and let stand overnight. Pour off the clear alcohol solution through a small tared filter paper into a second funnel. Treat the semi-solid oily residue in the first funnel with 20 cc. of quarter-normal alcoholic potassium hydroxide, shake vigorously, let stand for 30 min., and pour off the alcoholic solution through the filter, combining it with the alcohol solution from the first extraction. Wash the residue 3 times with 15-cc. portions of 96-per cent alcohol, filtering each wash solution and combining all the alcohol extracts.

The residue in the funnel consists of neutral oil, which may contain a small amount of highly polymerized compounds. Dissolve the residue in a mixture of 10 cc. of carbon tetrachloride and 10 cc. of acetone. Filter the solution through the filter used for the alcohol solutions into a weighed dish. Wash the funnel and paper with 5 cc. of carbon tetrachloride and add the washings to the solution in the dish. Evaporate the solvent, dry the residue at 100 to 105°C. for 30 min., cool in a desiccator, and weigh. The residue *A*₁ consists of neutral fatty matter.

If an appreciable amount of insoluble matter remains on the filter, the filter may be dried and weighed and the weight of insoluble residue, *A*₁, determined. This consists of polymerized fatty matter.

To the alkaline alcoholic solution add 15 cc. of water and 5 cc. of glacial acetic acid. Shake thoroughly with 40 cc. of petroleic ether, let the phases separate, and draw off the alcohol-acetic acid solution into a second separatory funnel. Repeat the shaking-out process twice with 25-cc. portions of petroleic ether. Save the alcohol-acetic acid solution. Combine the petroleic ether extracts, and extract them 3 times with a mixture of 10 cc. of normal potassium hydroxide solution and 10 cc. of 70-per cent alcohol. Finally free the petroleic ether solution from alkali by shaking once with 9 cc. of 70-per cent alcohol and 1 cc. of hydrochloric acid (1:10), discard the acid wash solution, transfer the petroleic ether solution quantitatively to a tared dish, and evaporate, dry, cool, and weigh as above described. The residue *A*₂ also consists of neutral fatty matter. Calculate the combined percentage of *A*₁ and *A*₂ and report as neutral fats.

Treat the alcoholic potassium hydroxide solution, used for extracting the petroleic ether solution above, with 200 cc. water and 30 cc. of hydrochloric acid (1:10), and extract 3 times with 10-cc. portions of carbon tetrachloride. Combine the extracts in a tared dish, evaporate the solvent, and dry and weigh the residue as usual. The residue *B* consists of fatty acids. Calculate as percentage of the oil sample taken.

Treat the alcohol-acetic acid solution, from which neutral oil and fatty acids were extracted by petroleic ether as above described, with 100 cc. of water, and 35 cc. of concentrated hydrochloric acid. Previous to adding the water and acid the volume should be almost exactly 110 cc. if the directions have been followed, and the success of the ensuing extraction depends

upon the closeness with which the prescribed conditions are adhered to. Shake the solution vigorously with 10 cc. of carbon tetrachloride, let stand till separation takes place, draw off the carbon tetrachloride solution into a weighed dish, and reextract the solution 3 times with 7-cc. portions of carbon tetrachloride. Evaporate the solvent, and dry and weigh the residue as usual. The residue *C* consists of the sulfonated compounds. Calculate as percentage.

A further small quantity of fat may be recovered from the final acid-alcohol solution by evaporating it to 25 per cent of its bulk and reextracting with carbon tetrachloride. The residue so recovered is called *D*. The sum of all the residues accounts for about 95 per cent of the total fatty matter in the oil.

Henrich, working in the authors' laboratory, applied the Schindler-Schacherl separation to sulfonated neat's-foot and cod oils. He confirmed Schindler's observation that the residues A_1 and A_2 are nearly free from sulfur and from fatty acids, while *B* is rich in fatty acids, and *C* in sulfur compounds. Little or none of the fraction A_3 was encountered in this work. The percentages found for (A_1 plus A_2), *B*, and *C*, were quite reproducible, but those obtained for A_1 and A_2 , considered separately, were not.

STABILITY OF EMULSION

Measure with a graduated cylinder 10 cc. of the oil, and make up to 100 cc. with water. A stable emulsion should form almost spontaneously, milky if the oil is not completely neutralized, or almost optically clear if neutralization is complete. Let the emulsion stand for 24 hr.; no oil should separate in that time. Report the stability and character of the emulsion in appropriate terms.

pH VALUE OF EMULSION

Determine the pH value of the above emulsion as described in Chap. VII. Report pH value of a 10-per cent emulsion.

ANALYSIS OF SOAP (1, 5, 23, 49)

Soap is used as an emulsifying agent for animal and vegetable oils in fat liquors (54) and for waxes in finishes. The qualities which must be possessed by a soap that is to be used for such purposes are somewhat different from those of a soap to be used as a cleansing agent. In both fat liquoring and finishing, most of the fatty constituents of the soap are absorbed by the leather, and hence the nature of the fat contained in the soap is just as important as that of the unsaponified oils added to the leather. For this reason, the investigation of the fatty acids of soap is of

great importance. Equally important is the determination of the alkali, both free and combined, which the soap contains. As all leathers are slightly acid in character, the fat liquor must contain a certain reserve of alkalinity in order that the emulsion may not break so soon as to cause the oils to be deposited on the surface of the skins. On the other hand, the alkalinity must not be too great, or the emulsion will be too stable; excessive alkalinity also causes damage to the leather. In many fat liquors, part of the alkalinity is supplied by the soap used, and part by sodium carbonate or similar compounds. The alkali content of the soap must remain constant, or the whole operation may be upset completely.

Soap is composed of the sodium or potassium salts of fatty acids or, in some cases, of the resinic acids. A soap may contain, as by-products from inexact saponification, an excess of free alkali or of unsaponified fat or free fatty acids. Many soaps contain alkaline fillers, such as sodium carbonate, sodium silicate, sodium phosphate, or borax. Besides these active constituents, soap contains various inert substances. Water is always present. Neutral salts such as sodium chloride or sulfate may remain from the salting-out operation. Unsaponifiable matter is often introduced with the fat employed. Insoluble inorganic substances, such as talc or sand, classified as abrasives, and insoluble organic fillers, such as starch, may be encountered. Certain laundry soaps contain naphtha, and toilet soaps contain a wide variety of materials such as glycerol, alcohol, perfumes, dyes, etc., but these last are not likely to concern the leather manufacturer.

In general, it may be said that the soaps best suited to tannery use are the relatively pure soaps, made from pure animal and vegetable oils, free from alkaline or inert fillers and from rosin. For fat liquoring light leathers, a soap yielding fatty acids of low melting point is desirable, since fatty acids that are solid at room temperatures produce spews. Easily oxidizable fatty acids are objectionable for light-colored leathers, and the presence of much rosin is generally objectionable, since rosin acids have no lubricating properties and impart a tacky feel to the leather.

Since the analysis of soap is time consuming and expensive, the wisest course is to use only soaps of nationally known brands, that have been found satisfactory in practice. If this course is followed, it will be found sufficient to perform only an occasional analysis.

The average composition of samples of three typical soaps analyzed in the authors' laboratories during the past 10 years is given in Table 54 (54).

TABLE 54.—COMPOSITION OF TYPICAL SOAPS USED IN FAT LIQUORING

Constituent	Hard tallow soap	Castile soap	Fig soap
Water.....	19.6	23.0	45.8
Fatty acid anhydrides.....	65.4	58.7	39.3
Rosin.....	3.3	2.7	3.6
Free oil.....	0.2	0.2	0.8
Combined sodium oxide, Na_2O	9.0	9.1	0.0
Combined potassium oxide, K_2O	0.0	0.0	8.9
Sodium carbonate.....	0.2	0.8	0.0
Potassium carbonate.....	0.0	0.0	1.1
Sodium chloride.....	0.8	0.7	0.1
Fatty acids:			
Melting point $^{\circ}\text{C}$	38	14	13
Iodine value.....	39	55	99

WATER

Water is determined by drying and determining loss in weight. In the case of soaps containing easily oxidizable fats, the drying must be done in a vacuum oven (at least 20 in.) at not over 70°C . Or an inert atmosphere may be used at 105°C . This procedure is prescribed in the methods of the American Chemical Society (5). Many authors advise that about 10 g. of ignited sand and a short glass stirring rod be introduced and weighed with the dish. At hourly intervals the dish is removed from the oven and the cake broken up with the stirring rod to facilitate drying.

Oven Method.—Weigh accurately about 5 g. of soap into a weighed porcelain or glass dish 6 to 7 cm. in diameter and about 4 cm. deep. Place in an oven at 105°C ., and dry for 3 hr. Cool in a desiccator, and weigh. Replace the dish in the oven for 1 hr. longer, and reweigh. Repeat until the loss in weight on heating for 1 hr. does not exceed 5 mg. Calculate and report percentage of water.

$$\text{Per cent H}_2\text{O} = \frac{\text{g. loss in weight} \times 100}{\text{g. sample}}$$

Rapid Method.—Weigh accurately about 5 g. into a weighed porcelain dish containing a short glass rod (weighed with the dish). Heat gently

with constant stirring on an asbestos gauze over a free flame until no more moisture collects on a cold watch glass held over the dish. Cool in a desiccator, and weigh. Calculate percentage of loss in weight, and report as water.

TOTAL FAT

Total fat may be taken as the sum of unsaponifiable matter, free (neutral) fat, free fatty acids, combined fatty acids, and resin acids, each of which is determined separately in any case, or directly by the procedure given below.

Weigh accurately about 5 g. of soap, and dissolve in about 100 cc. of hot water. Transfer the solution to a separatory funnel, rinse the beaker with hot water, and let the solution stand till cool. Add an excess of dilute hydrochloric acid. Add about 50 cc. of ethyl ether, and shake. Let stand till complete separation has taken place and the water layer is clear (except for insoluble fillers). Draw off the water layer, and wash the ether layer with successive small quantities of water until the last wash water no longer reacts acid to methyl red. Transfer the ether solution to a glass evaporating dish, rinse the funnel three times with about 10 cc. of ether, let the ether evaporate at room temperature, and dry the dish and residue in an oven at 105°C. for 30 min. Cool in a desiccator, and weigh. Repeat until the loss on heating for 30 min. does not exceed 5 mg. Calculate and report percentage of total fat.

$$\text{Per cent total fat} = \frac{\text{g. residue} \times 100}{\text{g. sample}}$$

UNSAPONIFIED FAT AND UNSAPONIFIABLE MATTER

Unsaponified fat and unsaponifiable matter are extracted together from an aqueous solution of the soap, with either petroleic or ethyl ether. The latter is prescribed in the standard methods of the American Chemical Society (5). The combined extracted material is saponified, and the unsaponifiable matter then determined by a second extraction. Unsaponified fat is then determined by difference.

Weigh accurately about 5 g. of soap, and dissolve in about 100 cc. of 50-per cent alcohol, previously rendered just alkaline to phenolphthalein with tenth-normal sodium hydroxide. If the resulting soap solution is acid, titrate with tenth-normal sodium hydroxide until the solution becomes a very faint pink, in order to neutralize any free fatty acids, which would otherwise be extracted by petroleic ether. Transfer the solution quantitatively to a separatory funnel, and dilute to about 250 cc. with water. Add about 100 cc. of petroleic ether (b. p. 40 to 60°C.), and shake vigorously. Let stand until complete separation takes place. Draw off the water layer, preserving it for the determination of fatty acids and rosin (see below). Wash the petroleic ether layer about 3 times with small portions of water,

adding the washings to the main aqueous solution. Pour the petroleic solution through a dry filter paper into a weighed glass flask holding ~~also~~ 100 cc. Rinse the funnel 3 times with small quantities of petroleic ether. Let the petroleic ether evaporate at room temperature, or distill most of the solvent on a water bath. Heat the flask and residue in an oven at 105 C. for $\frac{1}{2}$ hr., cool in a desiccator, and weigh. Repeat till the loss in weight on heating for 30 min. does not exceed 5 mg. From the weight of petroleic ether-soluble matter obtained, calculate percentage of unsaponified fat plus unsaponifiable matter.

Now saponify the residue in the flask by treating it with alcoholic potassium hydroxide under a reflux condenser, as described under determination of unsaponifiable matter in oils. Transfer the solution to a separatory funnel, and extract the unsaponifiable matter with petroleic ether, as described above. Separate, wash, filter, evaporate, and dry as described in the preceding paragraph, and calculate percentage of unsaponifiable matter from the weight of petroleic ether residue obtained after saponification. Subtract the second residue from the first, and take the difference as unsaponified fat.

$$\text{Per cent unsaponifiable matter} = \frac{\text{g. second residue}}{\text{g. sample}}$$

$$\text{Per cent unsaponified fat} = \frac{(\text{g. first residue} - \text{g. second residue})}{\text{g. sample}} \times 100$$

FATTY ACID ANHYDRIDES

On acidifying the aqueous solution of soap obtained in the determination of unsaponified and unsaponifiable matter, the fatty acids and resin acids are set free and may be extracted with ether. The weight of ether-soluble matter so obtained, minus resin acids and free fatty acids, which are determined separately, gives the weight of fatty acids originally combined with alkali in the soap. If combined alkali is calculated as sodium oxide, the fatty acids should be calculated as anhydrides, obtained by multiplying the weight of fatty acids by 0.97.

Place the aqueous solution of soap obtained in the determination of unsaponified and unsaponifiable matter in a large separatory funnel. While twirling the funnel briskly, add exactly 25 cc. of normal hydrochloric acid. Add about 100 cc. of ethyl ether, shake, and let stand till complete separation takes place. Then draw off the water layer and wash the ether layer with small quantities of water until the last portion is no longer acid to methyl red. Combine the aqueous layer and washings, and save the solution for the determination of total alkali.

Pour the ether layer through a dry filter into a weighed glass evaporating dish, rinse the funnel and filter paper 3 times with a little ether, and evaporate the ether at room temperatures. Place the dish and fatty acids in an oven at 100°C. for 30 min., then cool for exactly 15 min. in an individual desiccator, and weigh. Repeat till the loss in weight on heating 30 min.

amounts to less than 5 mg. Calculate percentage of resin acids plus fatty acids.

$$\text{Per cent resin acids plus fatty acids} = \frac{\text{g. residue} \times 100}{\text{g. sample weighed for unsaponified matter determination}}$$

Determine resin acids and free fatty acids as described below. Subtract percentage of resin acids plus percentage of free fatty acids from the percentage found above, and calculate the difference as percentage of fatty acid anhydrides by multiplying by 0.97.

$$\text{Per cent fatty acid anhydrides} = (\text{per cent resin acids plus fatty acids} - \text{per cent resin acids} - \text{per cent free fatty acids}) \times 0.97.$$

FREE FATTY ACIDS

If the soap contains free fatty acids, the absolute alcohol solution of soap obtained in determining fillers (see below) will react acid toward phenolphthalein. In such a case, titrate the solution to the production of a faint pink color, using tenth-normal sodium hydroxide. Calculate and report percentage of free fatty acid as oleic acid.

$$\text{Per cent free fatty acid (as oleic)} = \frac{\text{cc. 0.1-N NaOH} \times 2.82}{\text{g. sample weighed for fillers}}$$

ROSIN

When a mixture of resin acids and true fatty acids is boiled with a mixture of absolute alcohol and sulfuric acid, the fatty acids are converted to their ethyl esters, which react neutral to phenolphthalein, while the resin acids are not affected. The esters and unaltered resin acids may be freed from the sulfuric acid by extracting with ether and washing the ether solution with 10-per cent sodium chloride solution. The resin acids may then be determined by titration in the ether solution.

The procedure given below is based on the above facts. The method was originated by Wolf. The standard method of the American Chemical Society (5) differs from the procedure given only in that the determination is carried out on a fresh portion of soap from which the fatty acids are obtained just as described under determination of fatty acid anhydrides, instead of on the fatty acids obtained in that determination.

Wolf Method.—Dissolve the residue obtained in the determination of fatty acid anhydrides in 20 cc. of absolute ethyl alcohol. Transfer the solution to a small flask equipped with reflux condenser. Add 20 cc. of a mixture of 1 part sulfuric acid and 4 parts absolute ethyl alcohol, and boil the mixture under the reflux condenser for 1 hr. Transfer the solution to a large separatory funnel, add about 100 cc. of a 10-per cent solution of sodium

chloride, and then shake with about 50 cc. of ethyl ether. After the separation of the layers has taken place, draw off the aqueous phase into a funnel, and reextract with ether. Draw off the water layer into a third funnel, and extract a third time with ether. Combine the three ether solutions, and wash them with small portions of 10-per cent sodium chloride solution until the last portion is no longer acid to methyl red indicator. Transfer the washed ether solution to a titrating vessel. Add an equal volume of neutral 95-per cent alcohol, and titrate with tenth-normal sodium hydroxide, using phenolphthalein indicator, to the production of a faint pink color. Calculate and report percentage of rosin.

Percent rosin = $\frac{3.46 \times \text{cc. } 0.1\text{-N NaOH}}{\text{g. sample weighed for determination of fatty acid anhydrides}}$

TOTAL ALKALI

In the determination of fatty acid anhydrides, the fatty acids were liberated by treating the aqueous solution of the soap with a measured excess of standard hydrochloric acid. By titrating the excess hydrochloric acid in the aqueous solution separated from the ether solution of the fatty acids, total alkali may be determined.

Titrate the aqueous solution obtained in the determination of fatty acid anhydrides with normal sodium hydroxide, using methyl orange indicator. Subtract the volume of alkali required from the volume of normal hydrochloric acid added to liberate the fatty acids. The difference is the volume of normal acid consumed in neutralizing the alkali of the soap. Calculate and report percentage of total alkali as sodium oxide, Na_2O .

Per cent total alkali $\text{Na}_2\text{O} = \frac{(25 - \text{cc. } 1\text{-N NaOH}) \times 3.1}{\text{g. sample weighed for determination of fatty acid anhydrides}}$

COMBINED ALKALI

Besides alkali combined with fatty acids to form soap, the soap may contain free lye or alkaline salts. The former is determined by titration of an absolute alcohol solution of the soap obtained in the determination of fillers, and the latter by titration of a water solution of the material insoluble in absolute alcohol.

Subtract from percentage of total alkali the sum of the percentages found for free lye (calculated as sodium oxide, Na_2O) and total alkalinity of matter insoluble in alcohol (calculated as sodium oxide). Report the difference as combined alkali as sodium oxide.

Per cent combined $\text{Na}_2\text{O} = \text{per cent total } \text{Na}_2\text{O} - (\text{per cent free NaOH} \times 0.775) - \text{per cent } \text{Na}_2\text{O} \text{ insoluble in } \text{C}_2\text{H}_5\text{OH}$

NOTE.—In the case of a potassium soap (soft soap or tig soap), the alkaline constituents should be calculated as potassium oxide. The following factors are useful:

$$\begin{aligned}K_2O &= Na_2O \times 1.52 \\K_2CO_3 &= Na_2CO_3 \times 1.30 \\KOH &= NaOH \times 1.40\end{aligned}$$

TOTAL SOAP

Total soap is found by adding the percents obtained for fatty acid anhydrides, rosin, and combined alkali.

Per cent total soap = per cent fatty acid anhydrides +
per cent rosin + per cent combined Na_2O

A rapid method for determining total anhydrous soap directly (as well as combined alkali at the same time) is afforded by the standard method of the American Chemical Society (5). In this method, the fatty acids are separated quantitatively and treated with exactly the amount of sodium hydroxide (potassium hydroxide in the case of soft soap) required to neutralize them. The soap so formed is dried and weighed. Corrections must be made for salts present in the added alkali and for unsaponified and unsaponifiable matter and free fatty acids.

A. C. S. Method (5).—Dissolve 5 to 10 g. of the soap, depending upon the anhydrous soap content, in 100 cc. of water in a 250-cc. Erlenmeyer flask. When solution is complete, add dilute sulfuric acid in slight excess, insert a small funnel in the neck of the flask, and heat the flask at a temperature not exceeding 60°C. until the fatty acids separate as a clear layer. Transfer to a separatory funnel, draw off the acid layer into a second separatory funnel, and shake the acid aqueous liquid with two 20-cc. portions of ethyl ether. Dissolve the fatty acids in the ether used for washing the aqueous liquid, and shake with 10-cc. portions of water until they are no longer acid to methyl orange. Unite the water portions used for washing, and shake with 20 cc. of ether. Wash this ether until the wash water is neutral to methyl orange. Save the acid water for the chloride determination. Unite the ether solutions (if necessary, filter, washing the paper with ether) in a suitable weighed vessel, add 100 cc. of neutral alcohol free from carbon dioxide, add phenolphthalein, and titrate to exact neutrality with standard sodium hydroxide solution. Evaporate off the alcohol, dry to constant weight as in the determination of matter volatile at 105°, and calculate the percentage of sodium soap. This soap naturally includes any mineral oil or neutral fat, which, if determined separately, must be deducted from the result to obtain the true soap. Calculate the combined sodium oxide, Na_2O , and deduct from the weight of soda soap to give the anhydrides. If the original soap was potash soap, proper calculation must be made to reduce to potassium oxide, K_2O , or the titration made directly with standard potassium hydroxide. In case the soap shows an excess of free acid, proper correction must be made in calculating the combined alkali in the soap. A blank test should be made on the sodium or potassium hydroxide solution for neutral salts, and the proper correction made if necessary. With soaps

containing a large amount of soluble silicates and soap products, a high percentage of finely divided material insoluble in water, the foregoing procedure cannot be applied as given. In such cases the filtrate obtained in the determination of total matter insoluble in alcohol can be used after neutralizing any free acid or alkali. Evaporate off the alcohol on a steam bath, take up in water, and proceed as above.

FILLERS (MATTER INSOLUBLE IN ALCOHOL)

A pure soap contains practically no material that is insoluble in alcohol. Most high-grade commercial soaps, however, contain small quantities of alcohol-insoluble matter, consisting mostly of sodium carbonate. Many soaps contain large amounts of deliberately added fillers—alkaline salts, abrasives, or inert ingredients.

Fillers are determined by dissolving the dry soap in absolute alcohol and filtering off the insoluble matter, which is weighed and further examined as described in later paragraphs.

Weigh accurately about 10 g. of soap, and place in a porcelain dish in an oven at 105°C. for 1 hr. This treatment removes most of the water. Dissolve the dry soap in about 50 cc. of boiling absolute alcohol. Filter the hot solution through a quantitative filter paper, previously washed 3 times with alcohol, dried at 105°C., cooled in a weighing bottle in a desiccator, and weighed. Wash the insoluble matter on the paper with hot absolute alcohol until a few drops of filtrate give practically no residue when evaporated on a watch glass. Place the paper in a tared weighing bottle (open) in an oven at 105°C. for 1 hr., stopper the bottle, cool in a desiccator, and weigh. Take the increase in weight of the paper as total fillers, and calculate as percentage of the soap.

$$\text{Per cent fillers} = \frac{\text{g. matter insoluble in alcohol} \times 100}{\text{g. sample weighed}}$$

FREE LYE

Free sodium hydroxide (or potassium hydroxide), if present, is dissolved by alcohol along with soap in the preceding determination.

Test the soap solution obtained in the determination of fillers with phenolphthalein. If the solution is colorless, titrate with tenth-normal sodium hydroxide to the production of a pink color, and calculate the results as free fatty acid, as directed above. If the soap solution turns pink, titrate with tenth-normal hydrochloric acid till the color is discharged, then back-titrate with tenth-normal sodium hydroxide until a faint pink color is produced. From the net volume of acid consumed, calculate percentage of free alkali in the soap.

$$\text{Per cent free NaOH} = \frac{\text{cc. 0.1-N HCl} \times 0.40}{\text{g. sample weighed for determination of fillers}}$$

MATTER INSOLUBLE IN WATER

The further extraction with water of the matter insoluble in alcohol gives matter insoluble in water.

Extract the filter paper containing matter insoluble in alcohol with water at about 60°C. until the filtrate no longer reacts alkaline to methyl orange. Preserve the filtrate for the determination of total alkalinity of fillers. Place the paper and water-insoluble residue in a tared weighing bottle (open), heat at 105°C. in an oven for several hours, insert the stopper, cool in a desiccator, and weigh. Repeat to constant weight. Calculate percentage of matter insoluble in water. The original weight of the paper was obtained in determining matter insoluble in alcohol.

Per cent H_2O -insoluble matter =

$$\frac{\text{g. insoluble matter} \times 100}{\text{g. sample weighed for determination of fillers}}$$

TOTAL ALKALINITY OF MATTER INSOLUBLE IN ALCOHOL

Any alkaline salts present in the soap and insoluble in alcohol are dissolved by water in the determination of matter insoluble in water. They are then determined collectively by titration of the filtrate from matter insoluble in water. If the total amount of alkaline salts present is small, it is sufficient to calculate and report total alkalinity of fillers as percentage of sodium carbonate. In a pure soap this will amount to only 1 to 2 per cent. In soaps containing larger amounts of alkaline fillers, qualitative tests should be made for silicate, phosphate, and borate, and quantitative determinations carried out for such of these substances as may be present (5). Sodium carbonate is then calculated by difference from the total alcohol-insoluble alkali, or, if very exact results are required, carbonate is determined by the evolution method (5).

Add methyl orange indicator to the filtrate obtained in determining matter insoluble in water. Titrate with tenth-normal sulfuric acid, or normal if the weight of alcohol-insoluble matter exceeds 0.5 g. Calculate percentage total alkalinity of matter insoluble in alcohol as sodium oxide and as sodium carbonate.

Per cent alcohol-insoluble Na_2O =

$$\frac{\text{cc. } O.}{\text{g. sample weighed for determinations of fillers}}$$

$$\text{Per cent } Na_2CO_3 = \frac{\text{cc. } 0.1-N \text{ } H_2SO_4 \times 0.53}{\text{g. sample weighed for determination of fillers}}$$

ASH

Weigh accurately about 2 g. of soap into a weighed platinum dish. Heat gently over a free flame until the soap ignites, then supply only enough heat to maintain combustion until the mass is completely carbonized. When all organic matter is thoroughly charred, cool and extract the mass 4 times with 25-cc. portions of hot water. Filter each portion, collecting the filtrates in a small beaker. Return the paper to the dish, and ignite till all carbon is consumed. Evaporate the water extract to a small bulk, transfer the solution quantitatively to the dish, and evaporate to dryness. Dry the residue at 105°C., and weigh. Calculate percentage of ash.

$$\text{Per cent ash} = \frac{\text{g. ash} \times 100}{\text{g. sample}}$$

CHLORIDES (AS SODIUM CHLORIDE). SULFATES (AS SODIUM SULFATE)

Sodium chloride or sodium sulfate may be present in soap as a result of the "salting-out" operation in manufacture. They may be determined in aliquots of a solution of the ash.

Dissolve the ash obtained as above in hot water, and make up to 250 cc. in a volumetric flask. Pipette 100 cc. into a beaker, and just acidify with dilute acetic acid. Then add a few drops of potassium chromate indicator, and titrate with tenth-normal silver nitrate to the formation of a brick-red precipitate of silver chromate. Calculate percentage of sodium chloride.

$$\text{Per cent NaCl} = \frac{\text{cc. 0.1-N AgNO}_3 \times 0.5846 \times 2.5}{\text{g. sample weighed for ash determination}}$$

Pipette 100 cc. of the ash solution into a beaker, and acidify with hydrochloric acid. Filter if necessary, and determine sulfate by precipitation with barium chloride as described under determination of sulfate in sulfonated oils by the gravimetric method. Calculate percentage of sodium sulfate.

$$\text{Per cent Na}_2\text{SO}_4 = \frac{\text{g. BaSO}_4 \times 60.86 \times 2.5}{\text{g. sample weighed for ash determination}}$$

EXAMINATION OF FATTY ACIDS

The foregoing determinations enable the analyst to report the composition of the soap in terms of water, unsaponifiable matter, neutral fat, combined fatty acid anhydrides, rosin, combined alkali, free lye, alkaline fillers, etc. They do not, however, give any information regarding the nature of the fat from which the soap was made—a point of very great importance to the leather chemist, since the fatty acids of the soap often become incorporated with the leather and influence the properties of the leather just as do the non-saponified oils used in fat liquoring. To

determine the nature of the fatty constituents, the soap is dissolved in water, unsaponifiable matter extracted from the solution with petroleum ether, and then the fatty acids are set free by acidulation. The fatty acids are extracted with petroleum ether, and the ether allowed to evaporate. Any of the determinations described under analysis of fats and oils may be carried out on the fatty acids so obtained. The most useful determinations, in the authors' judgment, are those of iodine value and melting point. The standard methods of the American Chemical Society (5) call for the determination of "titer" and acid value.

Authors' Method.—Dissolve about 5 g. of soap in about 125 cc. of 50-per cent ethyl alcohol. Extract unsaponified and unsaponifiable matter as previously described. Acidify the soap solution, and extract the liberated fatty acids with petroleum ether as described under determination of fatty acid anhydrides. Wash the ether solution free from acid, filter, and evaporate the solvent at room temperature. Dry briefly at 100°C.

Determine melting point and iodine value of the fatty acids by the methods given under analysis of fats and oils.

A. C. S. Method (5).—Dissolve about 50 g. of soap in 500 cc. of hot water, add 100 cc. of 30-per cent sulfuric acid, heat until the fatty matter collects in a clear layer, siphon off the acid layer, and wash the fatty matter free from acid with hot water. Decant the fatty matter into a dry beaker, filter, using a hot-water funnel or placing both the funnel and the receiving beaker in a water-jacketed oven, and dry for 20 min. at the temperature of boiling water.

When other determinations besides that of titer are to be made on the total fatty matter, and when volatile and readily oxidizable fatty acids are present, the following method should be used: Dissolve about 50 g. of the soap in 300 cc. of hot water, transfer to a separatory funnel, add 150 cc. of approximately twice-normal sulfuric acid, cool somewhat, add 120 cc. of ether, shake, draw off the acid layer, and wash the ether layer free from acid with strong salt, NaCl, solution. Then draw off the aqueous layer as completely as possible, transfer the ether layer to a flask (it is not necessary to transfer quantitatively), add 20 to 30 g. of anhydrous sodium sulfate, stopper the flask, shake, and let stand at a temperature below 25°C. until the ether layer becomes perfectly clear, showing that all water has been taken up by the sodium sulfate. Filter through a dry paper into another Erlenmeyer flask, and completely evaporate off the ether by passing through the flask a current of dry air and heating the flask to a temperature not above 50°C.

Determine titer on a portion of the fatty acids prepared as above by the method described under analysis of fats and oils.

Determine acid value as follows: In a 250-cc. Erlenmeyer flask dissolve about 2 g. of fatty acids, weighed accurately, in 20 to 30 cc. of neutral 95-per cent ethyl alcohol. Titrate with standard alkali, using phenolphthalein as indicator. Calculate the acid value (mg. of potassium hydroxide per gram of fatty acids).

ANALYSIS OF EGG YOLK (9, 45, 51)

The egg yolk sold to tanners for fat liquoring leather is usually the whole deshelled egg preserved either with salt or with borates. True egg yolk, separated from the white, is also on the market and is analyzed exactly like whole egg. Dried whole egg and dried egg yolk are sometimes employed.

The average composition of samples of whole egg analyzed in the authors' laboratories during the past 10 years is given in Table 55 (54). It will be noted that the composition of the salted egg yolk and the egg yolk preserved with borates is about the same except for water and sodium chloride. In preparing salted egg yolk, the manufacturer simply adds solid salt, while in preparing the "salt-free" material, the borate is added as a solution in an amount of water equivalent to the weight of salt added to the salted egg. Thus a given weight of either the salted or the salt-free product contains the same weight of actual egg, which is a convenience in price fixing and in using the materials.

The ratio of fat to albumin varies somewhat with the laying season. In true egg yolk, the ratio is considerably higher than that shown.

TABLE 55.—AVERAGE COMPOSITION OF COMMERCIAL EGG YOLK (WHOLE Egg)

Constituent	Salted	Salt free
Specific gravity at 15°C.....	1 140	1 038
Water.....	61 80	73 95
Fat (including lecithin and cholesterol).....	10 16	11 50
Unsaponifiable matter.....	0 24	0 32
Unoxidized fatty acids.....	8 68	9 51
Iodine value.....	68	71
Melting point, degrees centigrade.....	34	31
Oxidized fatty acids.....	0 28	0 44
Proteins (nitrogen \times 6.38).....	10 30	12 40
Ash.....	16 60	1 60
Sodium chloride.....	15 61	0 24
Sodium carbonate.....	0 19	0 27
Borates (as $\text{Na}_2\text{B}_4\text{O}_7$).....	0 68
Iron and aluminum (oxides).....	0 14	0 09
Calcium (as oxide).....	0 14	0 03

WATER

Weigh accurately about 5 g. of egg into a weighed platinum dish. Place in an oven at not over 105°C., and heat overnight. Cool for exactly 15 min. in an individual desiccator over fresh concentrated sulfuric acid. Weigh as rapidly as possible, since the dried residue is very hygroscopic. Replace the dish in the oven for 1 hr., cool as before, and reweigh. Repeat to constant weight. Take the loss in weight at 105°C. as water, and calculate and report in percentage.

$$\text{Per cent H}_2\text{O} = \frac{\text{g. loss in weight} \times 100}{\text{g. sample weighed}}$$

ASH

Heat the residue obtained in the determination of water over a small flame until it is completely charred. Extract the charred mass with several 25-cc. portions of hot water, filter, and collect the filtrate in a small beaker. Return the filter paper to the dish, and ash the residue at dull red heat. This procedure is advisable because it is almost impossible to burn off all the carbon in the presence of much salt without heating so hot as to volatilize part of the salt. By the procedure given, most of the salt is removed from the material before the final ignition. Evaporate the solution to a small bulk, and transfer the residue quantitatively to the dish. Evaporate to dryness on the water bath, then heat at about 200°C. for 1 hr. Cool in a desiccator, and weigh. Calculate and report percentage of ash.

$$\text{Per cent ash} = \frac{\text{g. ash} \times 100}{\text{g. sample weighed for water determination}}$$

Analysis of Ash. Sodium Carbonate.—Add exactly 10 cc. of tenth-normal hydrochloric acid to the ash, and let stand for about 5 min. Add methyl orange indicator, and if the solution is not acid add 10 cc. more of tenth-normal hydrochloric acid. Rinse the solution into a beaker, dilute to about 100 cc., and titrate the excess acid with tenth-normal sodium hydroxide. Calculate percentage of alkalinity of the ash as sodium carbonate, deduct the percentage of alkalinity due to calcium (see below) and borax (if present), and report the difference as percentage of sodium carbonate in the ash.

$$\text{Per cent alkalinity as} = \frac{(10 - \text{cc. } 0.1-N \text{ NaOH}) \times 0.53}{\text{g. sample weighed for ash determination}}$$

$$\text{Per cent Na}_2\text{CO}_3 = \text{per cent alkalinity as Na}_2\text{CO}_3 - (\text{per cent CaO} \times 1.9) - (\text{per cent Na}_2\text{B}_4\text{O}_7 \times 0.52)$$

Iron and Aluminum.—Treat the residue in the dish used for the determination of ash with about 5 cc. of concentrated hydrochloric acid, and heat nearly to boiling, add the solution to that in which sodium carbonate was titrated as described above, and filter if necessary. Precipitate with ammonia, and weigh iron and aluminum as oxides in the usual way, as described under analysis of sodium chloride (Chap. VIII).

$$\text{Per cent (Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3) = \frac{\text{g. oxides} \times 100}{\text{g. sample weighed for ash determination}}$$

calcium as oxalate in the filtrate from iron and
and

$$\text{Per cent CaO} = \frac{\text{g. CaO} \times 100}{\text{g. weighed for ash determination}}$$

CHLORIDE

Weigh accurately about 1 g. of egg into a platinum dish, and heat gently until all organic matter is carbonized, as described under determination of ash. Take up the charred mass with hot water, and filter. If the residue on the filter paper until the solution passing through the filter no longer gives a precipitate on testing a few drops with silver nitrate solution. Combine the filtrate and washings, and add a few drops of phenolphthalein indicator. If the solution proves to be alkaline, acidify with dilute acetic acid. Add a few drops of potassium chromate indicator, and titrate with tenth-normal silver nitrate solution until a brick-red forms. Calculate and report percentage of sodium chloride.

$$\text{Per cent NaCl} = \frac{0.1-N \text{ AgNO}_3 \times \text{g. sample weighed}}{100}$$

BORATES

Borates, in the form of borax or boric acid, are often added to salt-free egg as a preservative. They are not likely to be encountered in salted egg, since their presence therein is superfluous. To save time, it is advisable to perform a qualitative test for boron, followed, if necessary, by the quantitative determination. The following methods are those of the Association of Official Agricultural Chemists (8).¹

Preliminary Test.—Acidify the sample with hydrochloric acid in the proportion of 7 cc. of strong acid to 100 cc. of sample. In the case of solid or pasty samples heat with enough water to make sufficiently fluid before acidifying. Immerse a strip of turmeric paper in the acidified liquid, and allow the paper to dry spontaneously. If borax or boric acid is present, the paper will acquire a characteristic red color, changed by strong ammonium hydroxide to dark blue green but restored by acid.

Confirmatory Test.—Make about 25 g. of the sample decidedly alkaline with lime water, and evaporate to dryness on a steam bath. Ignite the dry residue at a low red heat until all organic matter is thoroughly charred; cool; digest with about 15 cc. of water; and add strong hydrochloric acid, drop by drop, until the solution is distinctly acid. Immerse a piece of turmeric paper in the solution and allow it to dry without heat. In the presence of borax or boric acid, the color change will be the same as described under the preliminary test.

¹ X, 15, 16.

Quantitative Method (Official).—Make 10 g. of the material distinctly alkaline with sodium hydroxide solution, and evaporate to dryness in a platinum dish. Ignite the residue until the organic matter is thoroughly charred, avoiding an intense red heat; cool; digest with about 20 cc. of hot water; and add strong hydrochloric acid, drop by drop, until the reaction is distinctly acid. Filter into a 100-cc. volumetric flask, and wash with a little hot water; the volume of the filtrate should not exceed 50 to 60 cc. Return the filter containing any unburned carbon to the platinum dish, make alkaline by wetting thoroughly with lime water, dry on a steam bath, and ignite to a white ash. Dissolve the ash in a few cubic centimeters of dilute hydrochloric acid (1:3), and add to the liquid in the 100-cc. flask, rinsing the dish with a few cubic centimeters of water. To the combined solutions add about 0.5 g. of calcium chloride and a few drops of phenolphthalein indicator, then 10-per cent sodium hydroxide solution until a permanent light pink color is produced, and finally dilute to the mark with lime water. Mix, and filter through a dry filter. To 50 cc. of the filtrate add normal sulfuric acid until the pink color disappears, then add methyl orange indicator, and continue the addition of acid until the yellow color changes to pink. Boil for about 1 min. to expel carbon dioxide. Cool, and carefully add half-normal sodium hydroxide until the liquid assumes a yellow tinge, avoiding an excess of alkali. All the boric acid is now in the free state with no uncombined sulfuric acid present. Add about 10 g. of neutral mannitol (a volume of neutral glycerol equal to the volume of the solution may be substituted for the mannitol) and a few drops of phenolphthalein indicator; note the burette reading; and again titrate the solution with the standard sodium hydroxide until a pink color develops. Add a little more mannitol (or glycerol), and if the pink color disappears continue the addition of alkali until a pink color appears again. Repeat the alternate additions of mannitol and alkali until a permanent end point is reached. 1 cc. of half-normal sodium hydroxide solution is equivalent to 0.0124 g. of boric acid.

$$\text{Per cent borates as Na}_2\text{B}_4\text{O}_7 = \frac{\text{cc. 0.5-N NaOH} \times 5.05 \times 2}{\text{g. sample weighed}}$$

FAT

Fat is determined by extraction with chloroform. The material so extracted and weighed includes all or most of the lecithin and cholesterol of the egg. In determining fat, it is essential that the egg be thoroughly dried before beginning the extraction.

Place on a watch glass a pad of fat-free absorbent cotton big enough to absorb the egg sample without allowing any of it to soak through. Weigh about 10 g. of egg in a weighing bottle, pour the sample on to the cotton, and obtain the sample weight by reweighing the bottle. Dry the egg on the cotton at 100°C. Trim away and discard as much as possible of the cotton that is not impregnated with egg. Cut the remaining cotton and egg into pieces with clean shears, working on a large glazed paper and taking care

that none of the sample is lost. Place all the material in an extraction thimble, plug the thimble with a wad of cotton, and extract with chloroform in a Soxhlett apparatus for at least 8 hr. Filter the chloroform solution of the fat through a dry, quick-acting filter paper, and rinse out the flask and paper three times with small quantities of chloroform. Receive the filtered chloroform in a weighed glass flask. Distill off most of the chloroform on a water bath, allow the last traces to evaporate in the air, then heat the residue for exactly 30 min. at not over 105°C. in an oven. Cool in an individual desiccator for 15 min., and weigh. Repeat till the loss in weight on heating 30 min. is not more than 5 mg. Calculate and report percentage of fat in the

$$\text{Per cent fat} = \frac{\text{g. ch}}{\text{g. sample}} \times 100$$

Examination of Fat.—Saponify the fat obtained in each of duplicate determinations as described above, using the procedure described under determination of unsaponifiable matter in oil. Combine the 2 soap solutions in one separatory funnel. Determine *unsaponifiable matter*, *unoxidized fatty acids*, and *oxidized fatty acids* exactly as described for oils. Determine *iodine value* and *melting point* of the unoxidized fatty acids and of the unsaponifiable matter if an appreciable quantity of the latter is obtained.

ALBUMIN

Total nitrogen is determined by the Kjeldahl method and calculated as albumin by multiplying the percentage of nitrogen found by the factor 6.38.

Weigh accurately about 2 g. of egg into a Kjeldahl flask, and digest over a flame with 10 g. of anhydrous potassium sulfate, 30 cc. of concentrated sulfuric acid, and a small crystal of copper sulfate. Regulate the heat so that the sulfuric acid condenses in the neck of the flask and runs back. Continue heating until the solution is colorless (except for a faint blue due to the added copper). Cool, and add about 250 cc. of water, put in a small piece of unglazed porcelain, and connect the flask with a condenser by means of the distilling head shown in Fig. 5 (Chap. II). Connect the outlet of the condenser with a Vollhard nitrogen bulb containing 50.0 cc. of tenth-normal sulfuric acid, 2 drops of methyl red indicator, and enough water to seal the connection to the side bulbs. Add strong sodium hydroxide solution to the solution in the flask through the funnel carried by the stopper (Fig. 5) until a permanent precipitate of brown cupric hydroxide is formed. Heat to boiling, taking care that the initial ebullition is not so violent that alkali is carried over into the receiver by frothing, and distill until the contents of the flask begin to "bump," due to the increasing concentration of sodium salts in the solution. When this stage is reached, about 150 cc. of distillate should have been collected in the receiver. If a smaller quantity has been distilled, add 100 cc. of water to the solution in the flask, through the stop-cock funnel, and distill again to the bumping point. Disconnect the Vollhard bulb from the condenser, and titrate the excess acid with tenth-normal sodium hydroxide till the pink color is just discharged, being careful to mix

the solution in the side bulbs with that in the main flask after the latter is completely neutralized. Run a blank determination on the reagents used as described in Chap. II. Subtract the volume of alkali required to neutralize the excess acid and the volume of acid consumed in the blank from the volume of acid taken. Calculate the percentage of nitrogen in the egg as albumin.

$$\text{Per cent albumin } (N \times 6.38) = \frac{(50.0 - \text{cc. } 0.1-N \text{ NaOH} - \text{cc. } 0.1-N \text{ acid for blank}) \times 0.893}{\text{g. sample weighed}}$$

ANALYSIS OF USED FAT LIQUORS

The analysis of fat liquors may be required as a check on their preparation or to ascertain the changes taking place in the fat liquor during the fat-liquoring operation, in which case the liquor is analyzed before and after using. The determinations to be performed depend, of course, upon the particular ingredients that the fat liquor contains. The following determinations are useful in the case of the common oil-soap-alkaline salt fat liquor:

Unsaponifiable Matter.—Measure a volume of thoroughly mixed fat liquor containing about 3 g. of oil into a small flask. Place on the water bath until most of the water is expelled, then add 5 cc. of a 50-per cent solution of sodium hydroxide and 50 cc. of 95-per cent ethyl alcohol, and saponify as directed under determination of unsaponifiable matter in fatty oils. Extract unsaponifiable matter from the soap solution with petroleic ether, and weigh.

Unoxidized and Oxidized Fatty Acids.—Determine in the soap solution obtained above by the methods described under analysis of fatty oils.

Mineral Matter.—Evaporate 100 cc. of the fat liquor to dryness in a weighed platinum dish, ash the residue, and weigh.

Total Alkali.—Treat the ash with an excess of tenth-normal acid, and back-titrate the excess as described under soap analysis.

pH Value.—Determine by means of the hydrogen electrode, as described in Chap. VII.

References

1. "ALLEN'S Commercial Organic Analysis," 5th ed., vol. II, P. Blakiston's Son and Company, New York, 1924.
2. ALSOP, W. K., and L. A. CUTHBERT: Notes on Sulfonated Oil Analysis, *J. Am. Leather Chem. Assoc.*, **11**, 364-380, 1916.
3. ALSOP, W. K.: Analysis of Sulfonated Oils, *ibid.*, **12**, 266-278, 1917.
4. AMERICAN CHEMICAL SOCIETY: Standard Methods for the Sampling and Analysis of Commercial Fats and Oils, *Ind. Eng. Chem.*, **18**, 1,346, 1926.
5. AMERICAN CHEMICAL SOCIETY: Standard Methods for the Sampling and Analysis of Commercial Soaps and Soap Products, *ibid.*, **14**, 1,159-1163, 1922.
6. AMERICAN LEATHER CHEMISTS ASSOCIATION: Methods of Analysis, *J. Am. Leather Chem. Assoc.*, **22**, 567-593, 1927.

7. AMERICAN SOCIETY FOR TESTING MATERIALS: A. S. T. M. Standards, published triennially, 1927, Part II; A. S. T. M. Tentative Standards, 1928; Supplement to A. S. T. M. Standards, 1928, 1929.

8. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS: "Methods of Analysis," revised to December, 1924, 2d. ed., 1925; Changes in Methods of Analysis, *J. Assoc. Official Agric. Chem.*, **9**, 44-45, 1926; **10**, 35-36, 1927; **11**, 44, 1928; **12**, 44-46, 1929.

9. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS: Methods for the Analysis of Eggs and Egg Products, *J. Assoc. Official Agric. Chem.*, **9**, 56-59, 1926.

10. AUERBACH, M.: Analysis of Fats and Oils, *Collegium*, 302-303, 1928; abstracted *J. Am. Leather Chem. Assoc.*, **24**, 382, 1929.

11. AUERBACH, M.: Determination of Unsaponifiable Matter. Especially in Fish Oils and Wool Fat, *Collegium*, 374, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 532, 1926.

12. BAUER, K. H.: Estimation of Organically-combined Sulfuric Acid in Sulfonated Oils, *Chem. Umschau*, **35**, 25, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 142, 1929.

13. BUMCKE, C. G.: Analysis of Sulfonated Oils: Improvement of the Hart Method, *J. Am. Leather Chem. Assoc.*, **16**, 7-8, 1921.

14. BURTON, D., and R. G. F. SHAW: Bibliography of Oils, Fats, and Waxes, *J. Am. Leather Chem. Assoc.*, **24**, 196-212, 1929.

15. CLARKE, I. D.: Determination of Moisture in Tannery Materials, *J. Am. Leather Chem. Assoc.*, **21**, 385-398, 1926.

16. DAVIDSON, J.: Determination of Free Alkali in Soap, *Chem. Umschau*, **33**, 273, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 250, 1927.

17. FACHINI, S.: Analysis of Oils and Greases, *Cuir tech.*, **14**, 112, 1925; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 576, 1925.

18. ENGLIS, D. T., and V. C. MILLS: Determination of Saponification Value: A More Stable Alcoholic Potassium Hydroxide Reagent, *J. Assoc. Official Agric. Chem.*, **12**, 248-250, 1929.

19. FAUST, T. A., et. al.: Determination of Cold Test of Oils, *J. Am. Leather Chem. Assoc.*, **22**, 525-528, 1927.

20. GERMAN ASSOCIATION OF DÉGRAS AND LEATHER OIL MANUFACTURERS: Specifications for Degras and Leather Oil, *Gerber*, 81, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **21**, 535, 1926.

21. GILLET, MARCEL: Analysis of Soluble Oils and Greases, *Cuir tech.*, **15**, 305, 354, 1926; abstracted in *J. Am. Leather Chem. Assoc.*, **22**, 52, 1927.

22. GILLET, MARCEL, et. al.: Analysis of Oils and Fats, *J. Intern. Soc. Leather Trades Chem.*, **12**, 389, 1928; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 216, 1929.

23. GNAMM, HELLMUT: "Die Fettstoffe in der Lederindustrie. Mon. aus dem Gebiete der Fett-Chemie, Band VI," Wiss. Verlagsges. m. b. H., Stuttgart, 1926.

24. GRIFFIN, R. C.: "Technical Methods of Analysis," 1st ed., pp. 230-279, McGraw-Hill Book Company, Inc., New York, 1921.

25. HART, RALPH: Analysis of Sulfonated Oils, *J. Am. Leather Chem. Assoc.*, **12**, 550-558, 1917; *ibid.*, **14**, 90-92, 1919.

26. HART, RALPH: Determination of Total Saponifiable Matter in Sulfonated Oils by Difference, *J. Am. Leather Chem. Assoc.*, **15**, 495-498, 1920.

27. HART, RALPH: Determination of Inorganic Impurities in Sulfated Oils, *J. Am. Leather Chem. Assoc.*, **15**, 404-406, 1920; **16**, 159-161, 1921.
28. HART, RALPH: Determination of Neutral Fat in Sulfonated Oils, *J. Am. Leather Chem. Assoc.*, **24**, 120-121, 1929.
29. HARVEY, A.: "Practical Leather Chemistry," pp. 71-109, Crosby Lockwood and Son, London, 1920.
30. HERBIG, W.: Estimation of Sodium Sulfate in Sulfonated Oil, *Chem. Umschau*, **34**, 330, 1927; abstracted in *J. Am. Leather Chem. Assoc.*, **24**, 141, 1929.
31. HERTWIG, RAYMOND, referee: Report on Eggs and Egg Products, *J. Assoc. Official Agric. Chem.*, **9**, 348-354, 1926.
32. JAMIESON, G. S., referee: Report on Fats and Oils, *ibid.*, **9**, 247-253, 1926; **10**, 323-329, 1927; **11**, 301-308, 1928; **12**, 203-205, 1929.
33. KERN, E. J.: Determination of Sulfate in Sulfonated Oils, *Ind. Eng. Chem.*, **12**, 785, 1920.
34. KERR, R. H., and D. G. SORBER: Separation of Unsaponifiable Matter from Fats and Oils, *J. Assoc. Official Agric. Chem.*, **8**, 90, 1924.
35. LANG, G.: Determination of Ammonia in Sulfonated Oils, *Ind. Eng. Chem.*, **20**, 693, 1928.
36. LANGE, A. R.: Characteristics of Fish and Allied Oils, *ibid.*, **18**, 9, 1926.
37. LAST, E.: Analysis of Oxidized Oil, Moellon, and Dégras, *Collegium*, 329, 1924; abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 193, 1925.
38. LEVI, LOUIS E., and AUGUST C. ORTHMANN: "Laboratory Manual," pp. 33-46, Privately printed, Milwaukee, Wis., 1918.
39. MATHEWS, R. R.: Report of Joint Committee with the American Society for Testing Materials on Cold Test of Fatty Oils, *J. Am. Leather Chem. Assoc.*, **23**, 523-525, 1928; **24**, 242-244, 1929.
40. McNICOLL, D.: Estimation of Resin Acids in Fatty Mixtures, *J. Soc. Chem. Ind.*, **40**, 124T, 1921; abstracted in *J. Am. Leather Chem. Assoc.*, **17**, 185, 1922.
41. OBERFELL, C. R., et al.: Sulfonated Oil Analysis, *J. Am. Leather Chem. Assoc.*, **11**, 226-232, 1916.
42. ORTHMANN, A. C., and W. J. ARNER: Cold Test of Oils, *J. Am. Leather Chem. Assoc.*, **23**, 595-599, 1928.
43. PALMER, J. C.: Methods for the Determination of Total Solids in Liquid Eggs and Powdered Dried Eggs, *J. Assoc. Official Agric. Chem.*, **9**, 354-358, 1926.
44. PRIEST, G. W.: Sulfonated Oils, *J. Am. Leather Chem. Assoc.*, **23**, 599-603, 1928.
45. PROCTER, H. R.: "Leather Industries Laboratory Book," pp. 281-350, E. & F. N. Spon, London, 1908; "Leather Chemists' Pocket Book," E. & F. N. Spon, London, pp. 139-169, 1912.
46. SCHULTZ, G. W.: Analysis of Sulfonated Oils, *J. Am. Leather Chem. Assoc.*, **13**, 190-192, 1918; **14**, 266-278, 1919.
47. SCOTT, W. W., ed.: "Standard Methods of Chemical Analysis," 4th ed. (rev.), vol. II, pp. 1108-1157b, D. Van Nostrand Company, New York, 1927.

48. STADLER, O.: Sulfonated Oils and Proposals for their Analytical Evaluation with Reference to Practical Use in the Leather Industry, *Collegium*, 284, 1923; abstracted in *J. Am. Leather Chem. Assoc.*, **19**, 608, 1924.
49. STANISLAUS, I. V. S., and P. B. MEERBOTT: "American Soap-maker's Guide," Henry Carey Baird & Co., Inc., New York, 1928.
50. STIASNY, E., and C. RIESS: Manufacture and Properties of Sulfonated Fish Oil and Sulfonated Neat's-foot Oil, *Collegium*, 498, 1925; *J. Am. Leather Chem. Assoc.*, **20**, 76-108, 1926.
51. STIASNY, E., ed.: "Gerbereichnisches Taschenbuch," 2d ed., Theodore Steinkopff, Dresden and Leipzig, 1929.
52. WAERDEN, H. V. D.: Analysis of Sulfonated Oils, *Collegium*, 36, abstracted in *J. Am. Leather Chem. Assoc.*, **20**, 533, 1925.
53. WELWART, N.: Determination of Ammonia in Oil and Fat tions, *Chem. Ztg.*, **44**, 719, 1920; abstracted in *J. Am. Leather Chem.*, **16**, 49, 1921.
54. WILSON, JOHN ARTHUR: "The Chemistry of Leather Manufacture," 2d ed., vol. II, A. C. S. Mon. Ser., The Chemical Catalog Company, Inc., New York, 1929.
55. SCHINDLER, WILLIAM, and R. SCHACHERL: Fractionation of Sulfonated Oils, *Collegium*, 255, 1928; *J. Intern. Soc. Leather Trades Chem.*, **14**, 344, 1930.

CHAPTER XII

COLORING, FINISHING, AND MISCELLANEOUS MATERIALS

DYESTUFFS

The coloring of leather is done almost entirely with synthetic dyestuffs, although a few natural dyestuffs are still used, generally in conjunction with coal-tar dyes. A very large number of dyes have been used successfully for dyeing leather. Wilson (11) has listed about 60 of the dyes in common use in the leather industry, their common names, structures, and properties. The chemical identification of an unknown dye is seldom required in practice, and methods for such identifications are quite outside the scope of this book. It is often necessary, however, for the leather chemist to determine to what class of dyes a given dye belongs so that its behavior upon solution and in contact with different types of leather can be foretold and also to determine the shade and depth of color produced by the dye, in comparison with other dyes previously employed.

Acid, Basic, and Direct Dyes.—Acid dyes are readily soluble in water. They are fixed by either chrome-tanned or vegetable-tanned leather without the use of a mordant. The depth of color produced by an acid dye is increased if the dye solution is rendered acid. On treatment of leather, dyed with an acid dye, with dilute sodium carbonate solution, the dyestuff shows a tendency to be extracted from the leather.

Basic dyes are soluble in water. The solubility is increased by acidification; on making the solution alkaline, the free base is precipitated. Basic dyes are not fixed by chrome leather unless the latter has been retanned with vegetable tanning materials. Basic dyes are precipitated by tannin; Procter (7) recommends a solution containing 10 per cent of tannin and 10 per cent of sodium acetate for making the test. Basic dyes give an insoluble lake when mixed with acid dyes.

Direct dyes are soluble in water, and, in general, the solubility is increased by alkali and decreased by acid, although there are

exceptions to this rule. Direct dyes are not fixed by vegetable-tanned leather but are fixed by chrome leather; the fixation is so vigorous that very little penetration occurs. Direct dyes can be mixed with basic dyes without causing a precipitate to form.

Tinctorial Power (11).—The test most commonly made on dyestuffs in tannery laboratories is that for tinctorial power. Reputable dye houses standardize their dyes to show a given tinctorial power by appropriate dilutions with dextrin, salt, or other inert materials. But the tanner often wishes to compare the tinctorial powers of new dyes or dyes made by different firms. The tinctorial power is measured in terms of the value of one dye of each color kept as a standard. The tests are usually made on carefully prepared pieces of the tanner's own leather, and the measurement made is that of the amount of unknown required to produce the same depth of shade as a fixed amount of the standard dye.

Dr. R. E. Rose has furnished the authors with the following details of the method used in his laboratories: First 2 solutions are made up containing 2 g. of dye per liter, one with standard dye and the other with the dye to be tested. These solutions are spotted on filter paper, and the depth of color produced gives a very rough approximation of the relative strengths of the two dyes. About 6 or 8 pieces of specially prepared leather, as nearly identical as possible, are used for the test. They are all cut to 0.1 sq. ft. in area. Each is put into a 1-qt. glass jar. One is covered with a standard solution of the standard dye. The others are covered in turn with solutions of the dye to be tested, of the same volume, but of increasing concentration so as to produce a series of dyeings ranging from a shade lighter to a shade darker than that produced by the standard dye. The jars are placed in a shaking machine and run for 45 min. The pieces of leather are removed and dried in a special dry-box. The depths of color produced are compared. If sufficient care is exercised to keep the conditions the same for all of the tests, the tinctorial power of the unknown can be measured to within 1 or 2 per cent of the value of the standard.

With some yellow dyes, the method is not quite so sensitive and may involve an experimental error of as much as 5 per cent. In such cases, the sensitivity of the method can be increased by adding to each dye solution a fixed amount of a standard blue dye which changes the color to green. The strength is then determined by the yellowness of the dyed leather sample.

Tanners are often required to produce new shades of color on leathers, and sometimes they desire to experiment with new dyes to produce their regular line of colors. With a set-up

similar to that just described, it is not very difficult to arrive at the proper mixture required to produce the desired shade.

MORDANTS AND STRIKERS

The mordants, or "strikers," used in blacking leather include ferrous sulfate, copper sulfate, and potassium bichromate. Ferrous sulfate and copper sulfate are obtainable in a form so pure that their analysis is hardly worthwhile. If desired, these materials may be analyzed by the methods described in any standard work on quantitative analysis. The analysis of potassium bichromate is described in Chap. X.

The two most important mordants used in dyeing leather are potassium titanium oxalate and potassium antimonyl tartrate (tartar emetic). These substances prevent vegetable tanning materials from bleeding into the dye solution and forming a precipitate with basic dyes. As these substances are complex and frequently of variable composition, it is advisable that they be analyzed completely.

TITANIUM POTASSIUM OXALATE

This salt is the chief titanium compound used as a mordant in dyeing leather because it is one of the few titanium compounds that do not require an excess of acid in order to prevent hydrolysis and precipitation of titanium hydroxide from their solutions. The materials marketed by different manufacturers under the name of titanium potassium oxalate, or under various trade names, differ considerably in composition, and for this reason a complete analysis of each shipment is advisable. The average composition of samples of titanium potassium oxalate which proved satisfactory in use, analyzed in the authors' laboratory during the past 10 years, is given in Table 56.

TABLE 56.—AVERAGE COMPOSITION OF COMMERCIAL TITANIUM POTASSIUM OXALATE

Water (loss at 100°C.).....	12.91
Titanium as oxide.....	21.12
Potassium as oxide.....	21.35
Sodium as oxide.....	2.48
Oxalates as C_2O_4	48.40
Iron and aluminum.....	None
Chlorides.....	Trace
Sulfate.....	Trace

Water.—Weigh accurately about 5 g. into a weighed platinum dish, and dry in an oven at about 105°C. overnight. Cool in a desiccator, and weigh rapidly. Repeat to constant weight. Calculate and report percentage of water.

$$\text{Per cent H}_2\text{O} = \frac{\text{g. loss at 105}^\circ\text{C.} \times 100}{\text{g. sample weighed}}$$

Calcium and Magnesium.—Ignite at dull red heat the residue obtained in the determination of water until all carbon is consumed. Treat the residue with dilute hydrochloric acid, transfer to a beaker, and boil until the residue is thoroughly disintegrated. Titanium will remain partly undissolved. Without filtering, make the solution just alkaline with ammonia to precipitate iron, aluminum, and titanium; filter; and wash until the wash water is free from chlorides. Determine calcium and magnesium in the filtrate as directed under the analysis of sodium chloride in Chap. VIII.

Solubility in Water.—Weigh exactly 10.000 g., and dissolve in several hundred cubic centimeters of water. The solution should contain only a very slight sediment.

Titanium (8, 10).—Filter the solution prepared in testing for solubility, receiving the filtrate in a 1,000-cc. flask, and wash the paper three or four times with water. If the amount of insoluble matter is appreciable, ignite the filter paper in a platinum dish, and fuse the residue with a small amount of potassium acid sulfate. Dissolve the fusion in about 50 cc. of 10-per cent sulfuric acid, filter if necessary, and add the solution to the main solution in the flask. Make up to 1,000 cc.

Test a portion of the solution for iron with potassium ferrocyanide.

Pipette 50 cc. of the solution into a beaker, dilute to about 200 cc., and add ammonia slowly until the solution is just alkaline to litmus paper. Filter at once without boiling. If iron is absent, wash the precipitate thoroughly with hot water, ignite in a weighed crucible, cool in a desiccator, and weigh as titanium dioxide. If iron is present, redissolve the precipitate, which need not be washed more than twice nor transferred completely to the paper, in the least possible amount of dilute hydrochloric acid, receiving the solution in the beaker used for the precipitation. Wash the paper with hot water. Add a few drops of methyl red indicator, and add dilute ammonium hydroxide, drop by drop, till the color just changes to yellow. Then add enough hydrochloric acid to just restore the red color. Saturate the solution with sulfur dioxide gas, and boil until titanous acid is precipitated. Filter, and wash the precipitate thoroughly with a dilute solution of sulfurous acid. Dry the precipitate, ignite, and weigh as titanium dioxide. Calculate and report percentage of titanium as oxide.

$$\text{Per cent TiO}_2 = \text{g. TiO}_2 \times 200$$

Iron and Aluminum.—Boil the filtrate from titanium until the odor of sulfur dioxide disappears. Add bromine water until the yellow color remains, then boil until the solution is colorless. Precipitate iron and aluminum as hydroxides, filter, wash, ignite, and weigh as oxides as described under the analysis of sodium chloride (Chap. VIII). Calculate and report

the combined percentage of aluminum and iron as oxides. If the amount of precipitate is considerable, iron and aluminum may be separated as described under sodium chloride in Chap. VIII.

Oxalate.—Weigh accurately about 0.5 g., and dissolve in about 500 cc. of water in a large casserole. Add 25 cc. concentrated sulfuric acid, and heat to 70 to 80°C. Titrate with approximately tenth-normal potassium permanganate, which has been standardized against pure sodium oxalate, until the solution becomes pink and remains so for several minutes. Calculate and report percentage of oxalates as the oxalate ion, C_2O_4 .

$$\text{Per cent} \quad \frac{\text{cc. approx. } 0.1\text{-}N \text{ KMnO}_4 \times \text{factor} \times 0.4402}{\text{g. sample weighed}}$$

Sulfate.—Weigh accurately about 5 g., and dissolve in about 200 cc. of water and 10 cc. of concentrated hydrochloric acid. Filter if the solution is not clear. Heat to boiling, and add a few drops of 10-per cent barium chloride solution. If an appreciable precipitate forms, add about 10 cc. of the barium chloride solution, drop by drop, and filter, ignite, and weigh as barium sulfate, as described under analysis of sodium chloride (Chap. VIII). Calculate and report percentage of sulfate as sulfur trioxide.

$$\text{Per cent SO}_3 = \frac{\text{g. BaSO}_4 \times 34.3}{\text{g. sample weighed}}$$

Chloride.—Weigh accurately about 5 g., and dissolve in about 200 cc. of water and about 5 cc. of concentrated nitric acid. Filter if the solution is not clear. Add a few drops of tenth-normal silver nitrate solution. If an appreciable precipitate forms, determine chloride quantitatively by the Vollhardt method described under analysis of lime liquors in Chap. VIII. Calculate and report percentage of chloride as chlorine.

$$\text{Per cent Cl} = \frac{0.1\text{-}N \text{ AgNO}_3 \times 0.3546}{\text{g. sample weighed}}$$

Sodium and Potassium (8).—Sodium and potassium are first separated from other metals and weighed as their mixed chlorides. The separation of sodium from potassium may then be made either by the perchlorate or by the chlorplatinate method.

Weigh accurately about 1 g., and dissolve in about 200 cc. of water. Do not filter. Make the solution slightly acid with hydrochloric acid. For each per cent of sulfate present, add 0.2 cc. of 10-per cent barium chloride solution, plus a few drops excess. Make the solution alkaline with ammonia, and add about 10 cc. of 10-per cent ammonium carbonate solution. Allow the precipitate to settle. Filter through rapid filter paper, and wash several times with hot water. Dissolve the material on the filter with about 10 cc. of dilute hydrochloric acid, and receive the solution in the beaker used for the precipitation. Wash the filter several times with hot water. Reprecipitate with ammonia and ammonium carbonate as before, filter, and wash the precipitate free from chlorides. This double precipita-

tion is necessary because the first precipitate occludes sodium and potassium. Combine the two filtrates, and evaporate the solution to a small bulk. Transfer the solution quantitatively to a weighed platinum dish. Evaporate to dryness, preferably on a water bath to avoid danger of spattering, and heat the residue at a temperature below red heat until all ammonium salts are expelled. Cool in a desiccator, and weigh the residue, which consists of the chlorides of sodium and potassium. Calculate percentage of sodium chloride plus potassium chloride.

$$\text{Per cent NaCl + KCl} = \frac{\text{g. cnl}}{\text{g. sample weighed}}$$

Perchlorate Method for Potassium.—Dissolve the chlorides in a little water, and add about 0.25 g. of perchloric acid for each gram of chloride weighed above. Evaporate on the water bath, with stirring, to a syrupy consistency. Add a little hot water, and evaporate again till heavy fumes of perchloric acid are evolved. Cool. Add 20 cc. of 97-per cent alcohol containing 0.2-per cent perchloric acid, and stir thoroughly. Allow the precipitate to settle, and decant the alcohol through a Gooch crucible, previously dried at 130°C. and weighed. Wash the precipitate once by decantation with the alcohol-perchloric acid solution. Dissolve the precipitate in a little hot water, add about 0.5 g. of perchloric acid, and evaporate to fumes of perchloric acid. Wash once by decantation with the alcohol-perchloric acid solution, transfer the precipitate to the crucible, and wash four times with alcoholic perchloric acid and once with pure 97-per cent alcohol. Dry the crucible and precipitate at 130°C., and weigh. From the weight of potassium perchlorate obtained, calculate percentage of potassium chloride, and subtract from the percentage of mixed chlorides to obtain percentage of sodium chloride. Then calculate percentage of potassium as oxide and sodium as oxide.

$$\text{Per cent KCl} = \frac{\text{g. KClO}_4 \times 53.8}{\text{g. sample weighed}}$$

$$\text{Per cent NaCl} = \text{per cent (NaCl + KCl)} - \text{per cent KCl}$$

$$\text{Per cent K}_2\text{O} = \text{per cent KCl} \times 0.632$$

$$\text{Per cent Na}_2\text{O} = \text{per cent NaCl} \times 0.530$$

Chloroplatinate Method for Potassium.—Prepare a solution of ammonium chloride by adding about 5 g. of pulverized potassium chlorplatinate to 500 cc. of 20-per cent ammonium chloride solution, shaking at intervals throughout one day, letting the precipitate settle overnight, and decanting the clear solution. Prepare a solution of chlorplatinic acid containing 2.1 g. in 10 cc. (= 1 g. platinum).

Dissolve the mixed chlorides of sodium and potassium in a little water, add a few drops of concentrated hydrochloric acid, and add 15 cc. of platinum solution. Evaporate the solution on the water bath to a thick paste, take up the residue in 80-per cent alcohol, and filter through a Gooch crucible, previously washed with alcohol and dried at 100°C. Wash the precipitate with 80-per cent alcohol, continuing the washing several times after the washings become colorless. Then wash the precipitate 6 times

with the ammonium chloride solution. Wash again thoroughly with 80-per cent alcohol, dry at 100°C., and weigh. From the weight of potassium chloroplatinate obtained, calculate percentage of potassium chloride, and obtain the percentages of potassium oxide and sodium oxide as directed above under the perchlorate method.

$$\text{Per cent KCl} = \frac{\text{g. K}_2\text{PtCl}_6 \times 30.67}{\text{g. sample weighed}}$$

POTASSIUM ANTIMONYL TARTRATE (TARTAR EMETIC)

Tartar emetic is made by mixing antimony trioxide with potassium hydrogen tartrate, dissolving in hot water, and crystallizing. The formula is $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$. Common impurities are free tartaric acid, potassium hydrogen tartrate, and calcium salts. Potassium antimonyl oxalate is said to be added sometimes as an adulterant.

Total Antimony (8).—Prepare tenth-normal iodine solution as directed in Chap. XIII. Standardize the solution, which need not be exactly tenth-normal, against tenth-normal sodium thiosulfate solution which has been recently standardized against tenth-normal potassium dichromate.

Weigh accurately about 10 g. of tartar emetic, dissolve in water in a 500-cc. volumetric flask, and make to volume. Pipette exactly 25 cc. into an Erlenmeyer flask, and dilute to about 100 cc. Add 25 cc. of a 2-per cent solution of sodium bicarbonate. Add a few drops of starch indicator, and titrate with approximately tenth-normal iodine solution until a blue color is produced. Calculate and report percentage of antimony as potassium antimonyl tartrate.

$$\text{Per cent K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 0.5\text{H}_2\text{O} = \frac{\text{cc. 0.1-N iodine solution} \times \text{factor} \times 41.55}{\text{g. sample weighed}}$$

Free Tartaric Acid.—Pipette 50 cc. of the solution prepared for the determination of antimony into an Erlenmeyer flask, add a few drops of methyl red indicator, and titrate with tenth-normal sodium hydroxide to the production of a yellow color. Calculate and report percentage of free tartaric acid.

$$\text{Per cent free H}_2\text{C}_4\text{H}_4\text{O}_6 = \frac{0.1\text{-N NaOH} \times 7.50}{\text{g. sample weighed}}$$

Sulfate, Chloride, Oxalate, and Calcium.—Place portions of the tartar emetic solution in each of four test tubes, and acidify each with acetic acid. Test for sulfate by adding barium chloride solution, for chloride by adding silver nitrate solution, for calcium by adding a few drops of oxalic acid solution, and for oxalate by adding a few drops of calcium chloride solution. If any positive tests are obtained, determine the constituents quantitatively, employing a 50-cc. portion of the tartar emetic solution.

Insoluble Matter.—Weigh accurately about 5 g. and dissolve in 100 cc. water. If insoluble matter is present, filter through a Gooch crucible,

previously dried at 105°C. and weighed, wash 5 times with small quantities of water, dry at 105°C., and weigh. Calculate and report percentage of insoluble matter.

ORGANIC ACIDS

Formic, acetic, and lactic acids are used in many departments of the tannery where a weak acid is required. Oxalic acid is sometimes used for bleaching.

FORMIC ACID

The commercial material contains about 90 per cent formic acid and should be free from non-volatile matter, sulfuric, hydrochloric, oxalic, and acetic acids. In cold weather, crystals of formic acid are sometimes deposited from the solution, and for this reason the shipment must be brought to room temperature and stirred thoroughly before the sample is taken.

Specific Gravity.—Determine specific gravity with a pycnometer. The Geissler form shown in Fig. 81 is very convenient. First clean and dry the pycnometer, and determine its weight empty (W_1). Then fill it with water at a temperature below 60°F., insert the thermometer, thereby forcing the excess liquid out of the capillary, and allow the temperature to rise gradually. When the temperature is exactly 60°F., wipe off the end of the capillary with a clean cloth, and close the tube with the ground-glass cap. Weigh the pycnometer filled with water (W_2). Dry the pycnometer, and obtain its weight filled with formic acid (W_3) in the same way. Calculate and report specific gravity at 60°F.



FIG. 81.—
Pycnometer.

$$\text{Sp gr.} = \frac{W_3 - W_1}{W_2 - W_1}$$

The relation between specific gravity and concentration of formic acid is given in Table 57.

Total Acid as Formic Acid.—Pipette about 5 cc. of acid into a small glass-stoppered weighing bottle, previously weighed. Stopper and weigh the bottle and acid. Immerse the bottle in about 300 cc. of carbon dioxide-free water, remove the stopper with a glass hook, mix, fish out the bottle and stopper with a glass rod, and rinse them with a wash-bottle stream. Transfer the solution to a 1,000-cc. volumetric flask, make up to the mark with carbon dioxide-free water, and mix thoroughly. Pipette 25 cc. into an Erlenmeyer flask, and titrate with tenth-normal sodium hydroxide, using phenolphthalein indicator. Calculate percentage of total acid as formic acid.

$$\text{Per cent HCOOH} = \frac{\text{cc. 0.1-N NaOH} \times 18.40}{\text{cc. sample}}$$

TABLE 57.—SPECIFIC GRAVITY OF FORMIC ACID SOLUTIONS AT 15°C.

Per cent by weight	Specific gravity	Per cent by weight	Specific gravity
1	1.0025	35	1.0925
2	1.0050	40	1.1050
3	1.0075	45	1.1145
4	1.0100	50	1.1240
5	1.0125	55	1.1330
6	1.0150	60	1.1420
7	1.0175	65	1.1515
8	1.0200	70	1.1650
9	1.0225	75	1.1705
10	1.0250	80	1.1800
15	1.0390	85	1.1905
20	1.0530	90	1.2010
25	1.0665	95	1.2120
30	1.0800	100	1.2230

To find the true formic acid content, subtract from the result obtained above the equivalent of the sulfuric, hydrochloric, oxalic, or acetic acid that may be present.

1 per cent H_2SO_4	= 0.94 per cent HCOOH
1 per cent HCl	= 1.30 per cent HCOOH
1 per cent $\text{HC}_2\text{O}_3\text{O}_2$	= 0.77 per cent HCOOH
1 per cent $\text{H}_2\text{C}_2\text{O}_4$	= 1.02 per cent HCOOH

Non-volatile Matter.—Measure 50 cc. with a cylinder into a weighed platinum dish. Evaporate to dryness on the hot plate, cool, and weigh. Calculate percentage of non-volatile matter. Then ignite the dish over a flame, cool, and weigh. Calculate percentage of ash. Samples analyzed in the authors' laboratory have contained, as a rule, about 0.03 per cent non-volatile matter and less than 0.01 per cent ash. If the amount of ash is appreciable, test it for iron as described under analysis of water in Chap. VIII.

Acetic Acid: Qualitative Test.—Place 50 cc. of the solution prepared for the determination of formic acid in a porcelain dish, and treat with 1 or 2 g. of yellow mercuric oxide. Warm gently. Mercuric oxide reacts with formic acid, liberating carbon dioxide. When the reaction has subsided, evaporate to dryness on the water bath. To the residue add 10 cc. of water and 10 cc. of pure ethyl alcohol; then add concentrated sulfuric acid drop by drop until the dish is hot to the touch. If acetic acid is present, ethyl acetate will be evolved and will be detected by its fruity odor.

Quantitative Test.—If acetic acid is found by the above test, pipette 100 cc. of the formic acid solution into a 250-cc. distilling flask, add mercuric oxide as before, and warm. After the reaction is complete, make the solution acid with sulfuric acid, and distill the acetic acid in a current of steam,

receiving the distillate in a flask containing 50.0 cc. of tenth-normal sodium hydroxide. Back-titrate the excess sodium hydroxide using phenolphthalein indicator, and calculate percentage of acetic acid from the volume of alkali consumed. If chloride is present, deduct the equivalent of the hydrochloric acid from the result.

$$\text{Per cent HC}_2\text{H}_3\text{O}_2 = \frac{\text{cc. 0.1-N NaOH consumed} \times 0.6}{\text{g. sample in 100 cc. solution}}$$

Sulfate, Chloride, and Oxalate.—Test portions of the formic acid solution for sulfate, chloride, and oxalate with barium chloride, silver nitrate, and calcium chloride and ammonia, respectively. If one or more of these substances is present, determine it quantitatively by the usual methods, and calculate as the acid.

LACTIC ACID

Specific Gravity.—Determine with the pycnometer as described for formic acid, or with a hydrometer, as described under analysis of sulfuric acid in Chap. X.

Color.—Report color as “water white,” “light yellow,” “brown,” etc.

Ash, Iron, and Calcium Sulfate.—Weigh accurately about 5 g. into a weighed platinum dish. Heat over a flame in a good hood until all the acid is evaporated or destroyed, and ignite till the residue is white. Cool, weigh, and calculate percentage of ash. Fuse the ash with a little sodium carbonate, cool, decompose the fusion with dilute hydrochloric acid, and transfer the solution to a beaker. Dilute to about 150 cc., and boil to expel carbon dioxide. Determine iron as oxide and calcium as oxide, as described under the analysis of sodium chloride (Chap. VIII), and calculate and report percentage of iron as oxide and calcium as oxide.

$$\begin{aligned}\text{Per cent ash} &= \frac{\text{g. ash} \times 100}{\text{g. sample}} \\ \text{Per cent Fe}_2\text{O}_3 &= \frac{\text{g. Fe}_2\text{O}_3 \times 100}{\text{g. sample}} \\ \text{Per cent CaO} &= \frac{\text{g. CaO} \times 100}{\text{g. sample}}\end{aligned}$$

Free Sulfuric Acid (Method of the A. L. C. A.) (2).—Dissolve 50 g. of the sample in 200 ml. of neutral 95-per cent alcohol, heat to 60°C., cover, and let stand overnight in a warm place. Filter, and wash with alcohol. Evaporate the alcohol from the filtrate, make up the residue to 250 ml. with water, add 5 ml. of concentrated hydrochloric acid, boil, and add barium chloride solution. Determine the precipitated barium sulfate in the usual manner. Calculate to percentage of sulfuric acid on the original sample.

Volatile Acid (Method of the A. L. C. A.).—Dilute 1 g. of sample to about 50 ml. with water, and titrate with half-normal sodium hydroxide using phenolphthalein as indicator. Calculate to lactic acid (1 ml. of half-normal sodium hydroxide is equivalent to 0.045 g. of lactic acid). On the basis of

this determination make up a solution of the sample containing 15 g. of lactic acid per liter. Put 150 ml. of this dilution in a long-neck 300-ml. Kjeldahl flask, connected through a Kjeldahl bulb trap to a vertical spiral condenser. The total height from the bottom of the flask to the top of the turn connecting with the condenser shall be between 20 and 24 in. Distill over 125 ml. in from 47 to 53 min., counting from the time the first drop falls into the receiver, which should be a graduated cylinder. Add 125 ml. of water to the residue in the flask, and repeat the distillation. Titrate the distillates, either separately or collectively, with tenth-normal sodium hydroxide, using phenolphthalein as indicator, and calculate the total number of milligrams of acetic acid (1 ml. of tenth-normal sodium hydroxide is equivalent to 6 mg. of acetic acid). From this value for acid found in the distillates determine by means of the accompanying distillation table the actual weight of volatile acid originally in the distilling flask, and calculate it as percentage of volatile acid.

DISTILLATION TABLE (TWO DISTILLATIONS)

Quantity of volatile acid in distilling flask corresponding to quantity of acid found in distillates under conditions specified
(All values in milligrams)

In distillates	In flask	In distillates	In flask	In distillates	In flask	In distillates	In flask
5	0.0	22	19.2	39	38.9	56	58.6
6	1.0	23	20.4	40	40.0	57	59.8
7	2.0	24	21.5	41	41.1	58	61.1
8	3.0	25	22.7	42	42.3	59	62.3
9	4.0	26	23.9	43	43.4	60	63.5
10	5.0	27	25.0	44	44.6	61	64.7
11	6.2	28	26.2	45	45.7	62	65.9
12	7.4	29	27.3	46	46.8	63	67.2
13	8.6	30	28.5	47	48.0	64	68.4
14	9.8	31	29.7	48	49.2	65	69.6
15	11.0	32	30.8	49	50.3	66	70.8
16	12.1	33	32.0	50	51.5	67	72.0
17	13.4	34	33.1	51	52.7	68	73.3
18	14.5	35	34.3	52	53.9	69	74.5
19	15.7	36	35.4	53	55.0	70	75.7
20	16.9	37	36.6	54	56.2	71	76.9
21	18.1	38	37.7	55	57.4	72	78.1

Free Acid and Anhydride (Method of the A. I. C. A.).—Titrate 50 ml. of the dilution as made for Volatile Acid in the cold with half-normal sodium hydroxide and phenolphthalein to the first full pink. Call this the "first titration." From this value subtract the number of milliliters of half-normal sodium hydroxide equivalent to the sum of free sulfuric acid and volatile acid present in the 50-ml. aliquot. (If the sample contains free oxalic or

hydrochloric acid, the amount must be determined by appropriate analysis, and further deduction made.) Calculate the remainder to lactic acid, and express it as percentage of free lactic acid. After completing the first titration, add 4 ml. of half-normal sodium hydroxide in excess, or 5 ml. in the case of concentrated acid, and let stand at 20 to 25°C. for 15 min. Then add 5 ml. of half-normal sulfuric acid, boil, and titrate back with half-normal sodium hydroxide. Determine the quantity of alkali used by the anhydride, and calculate it to lactic acid. Express the result as percentage of lactic acid equivalent to anhydride present.

ACETIC ACID

Total Acid as Acetic Acid.—Dry and weigh a small glass-stoppered weighing bottle. Pipette about 6 cc. of glacial acetic acid, or proportionally more of the dilute acid, into the bottle, stopper, and weigh. Immerse the bottle in water, remove the stopper with a glass hook, mix, withdraw bottle and stopper with a glass rod, and rinse them with a wash-bottle stream. Transfer the solution to a 1,000-cc. volumetric flask, and dilute to the mark. Mix thoroughly. Pipette 50 cc. into a beaker, and titrate the acid with tenth-normal sodium hydroxide, using phenolphthalein indicator.

$$\text{Per cent HC}_2\text{H}_3\text{O}_2 = \frac{\text{cc. 0.1-N NaOH} \times 2.1}{\text{g. sample weighed}}$$

Sulfate, Chloride.—Test portions of the above solution with barium chloride and silver nitrate, respectively. If positive tests are obtained, determine the constituent found by the usual methods.

Formic Acid (8).—Weigh rapidly about 5 g. of glacial acetic acid, or proportionally more of the dilute acid, to the nearest 0.1 g. Place the acid in a small flask equipped with a reflux condenser. Add 5 g. of sodium acetate, 40 cc. of a 5-per cent solution of mercuric chloride, and 30 cc. of water. Heat the flask for 2 hr. on the steam bath. If a precipitate of mercurous chloride forms, formic acid is present. If the amount of precipitate is appreciable, filter the solution through a weighed Gooch crucible, wash 4 times with very small quantities of cold water, dry at 100°C., and weigh. Calculate and report percentage of formic acid.

$$\text{Per cent} \quad \text{HgCl} \times 9.77$$

Furfural.—Add to 100 cc. of the acid about 5 cc. of aniline dissolved in 2 cc. of pure glacial acetic acid. If furfural is present, a red color will be produced.

OXALIC ACID

Oxalates (as Oxalic Acid).—Weigh accurately about 5 g. of acid, and dissolve in water, transfer to a 500-cc. volumetric flask, and make up to the mark. Pipette 20 cc. into a casserole, and determine oxalate by titration with tenth-normal potassium permanganate, as described under the analysis of titanium potassium oxalate. Calculate and report percentage of oxalic acid.

$$\text{Per cent H}_2\text{C}_2\text{O}_4 = \frac{\text{cc. 0.1-N KMnO}_4 \times \text{factor} \times 22.505}{\text{g. sample weighed}}$$

Insoluble Matter.—If the solution prepared above is not completely clear, the solution may be filtered through a weighed Gooch crucible before making up to volume, washing the insoluble matter until the washings no longer react acid to methyl red. Dry the crucible at 100°C., cool, weigh, and calculate percentage insoluble matter.

$$\text{Per cent insoluble matter} = \frac{\text{g. insoluble matter} \times 100}{\text{g. sample weighed}}$$

Ash.—Weigh accurately about 5 g. of acid into a weighed platinum dish, and ash at dull red heat. Cool and weigh. Calculate and report percentage of ash. If the amount present is more than 0.1 per cent, analyze it as directed below.

$$\text{Per cent ash} = \frac{\text{g. ash} \times 100}{\text{g. sample}}$$

Neutral Oxalates.—Any neutral oxalates will appear as sodium carbonate in the ash. Treat the ash with exactly 10 cc. of tenth-normal sulfuric acid, let stand for a few minutes, wash the solution into a beaker, and heat to boiling to expel carbon dioxide. Cool, add a few drops of methyl red indicator, and titrate the excess acid with tenth-normal sodium hydroxide. From the volume of acid consumed, calculate percentage of neutral oxalate as sodium oxalate. Calculate percentage of oxalic acid equivalent to the sodium oxalate found, deduct from the total oxalate, and report the difference as oxalic acid.

$$\text{Per cent Na}_2\text{C}_2\text{O}_4 = \frac{\text{cc. 0.1-N H}_2\text{SO}_4 \times 0.67}{\text{g. sample weighed for ash determination}}$$

Iron, Aluminum, Calcium, and Magnesium.—Determine in the solution after titrating the sodium carbonate, by the methods described under the analysis of sodium chloride (Chap. VIII).

Sulfate, Chloride.—Test portions of the solution prepared for the determination of oxalate with barium chloride and with silver nitrate. If a positive test is obtained, determine the constituent found by the usual methods.

AMMONIA

Ammonia is used in many operations connected with the coloring and finishing of black leather. The commercial material contains about 28 per cent NH_3 and has a specific gravity of 0.90. The material should be practically free from non-volatile matter. In sampling and analyzing ammonia, the volatility of the substance should be remembered.

Specific Gravity.—Determine with the pycnometer, as described for formic acid, or with the hydrometer, using an instrument scaled for liquids lighter than water. Determine percentage of ammonia from the specific gravity by referring to Table 58.

TABLE 58.—SPECIFIC GRAVITY OF AQUA AMMONIA AT 60°F.
(According to W. C. Ferguson. Approved and adopted as standard by the
Manufacturing Chemists' Association of the United States, May 14, 1903)

Specific gravity	Per cent NH ₃	Specific gravity	Per cent NH ₃	Specific gravity	Per cent NH ₃
1.0000	0.00	0.9556	11.18	0.9150	23.52
0.9982	0.40	0.9540	11.64	0.9135	24.01
0.9964	0.80	0.9524	12.10	0.9121	24.50
0.9947	1.21	0.9508	12.56	0.9106	24.99
0.9929	1.62	0.9492	13.02	0.9091	25.48
0.9912	2.04	0.9475	13.49	0.9076	25.97
0.9894	2.46	0.9459	13.96	0.9061	26.46
0.9876	2.88	0.9444	14.43	0.9047	26.95
0.9859	3.30	0.9428	14.90	0.9032	27.44
0.9842	3.73	0.9412	15.37	0.9018	27.93
0.9825	4.16	0.9396	15.84	0.9003	28.42
0.9807	4.59	0.9380	16.32	0.8989	28.91
0.9790	5.02	0.9365	16.80	0.8974	29.40
0.9773	5.45	0.9349	17.28	0.8960	29.89
0.9756	5.88	0.9333	17.76	0.8946	30.38
0.9739	6.31	0.9318	18.24	0.8931	30.87
0.9722	6.74	0.9302	18.72	0.8917	31.36
0.9705	7.17	0.9287	19.20	0.8903	31.85
0.9689	7.61	0.9272	19.68	0.8889	32.34
0.9672	8.05	0.9256	20.16	0.8875	32.83
0.9655	8.49	0.9241	20.64	0.8861	33.32
0.9639	8.93	0.9226	21.12	0.8847	33.81
0.9622	9.38	0.9211	21.60	0.8833	34.30
0.9605	9.83	0.9195	22.08	0.8819	34.79
0.9589	10.28	0.9180	22.56	0.8805	35.28
0.9573	10.73	0.9165	23.04		

Ammonia.—Weigh about 5 g. of ammonia in a glass-stoppered weighing bottle as described for formic acid. Pipette exactly 100 cc. of normal sulfuric acid into a 1-l. beaker, dilute to about 800 cc., and immerse the weighing bottle containing ammonia in this solution. Withdraw the stopper, and mix thoroughly. Add methyl red indicator, and titrate the excess acid with normal sodium hydroxide. Calculate and report percentage of ammonia.

$$\text{Per cent NH}_3 = \frac{(100 - \text{cc. 1-}N \text{ NaOH}) \times 1.7}{\text{g. sample weighed}}$$

Non-volatile Matter.—Measure with a graduated cylinder 50 cc. of ammonia into a weighed dish, and evaporate to dryness under a hood. Cool and weigh. Calculate percentage of non-volatile matter. If the percentage found is appreciable, examine the residue as described under analysis of ash of vegetable-tanned leathers (Chap. II).

FINISHING MATERIALS

A very wide variety of materials are used in finishing different kinds of leather. Water finishes, as distinguished from lacquer finishes, which will be discussed later, generally contain one or more substances of each of the following classes: binders, waxes, pigments.

If leather is to be glazed, waxes may be dispensed with. In some cases, pigments may be omitted, in which case the finish may contain a dye, which may also be added to pigment finishes to adjust the color produced by the pigment.

The substances used as binders are numerous and diverse in character. The more important binders are classified below (11):

1. **Mucilages.**—These are carbohydrate substances of vegetable origin, including *linseed*, *Irish moss*, *algin*, *gum Arabic*, *gum tragacanth*, and *dextrin*.

2. **Shellac.**

3. **Proteins**, including *gelatin*, *casein*, *egg albumin*, and *blood albumin*.

The proteins are frequently rendered insoluble and waterproof by the addition of *formaldehyde*.

The wax most commonly used in finishing is *carnauba wax*. Other waxes that find some use in the leather industry are *beeswax*, *Japan wax*, and *candelilla wax*.

The *pigments* used in finishing commonly consist of mineral substances ground in sulfonated oil. For reds and browns, the various iron oxide pigments are used; for yellow, *chrome yellow*; for blue, *ultramarine* or *Chinese blue*; and these primary colors are combined to produce the innumerable shades of leather that are demanded. Often the color is adjusted by adding dyes. Other pigments, of a quite different type, are composed of *lakes*, or insoluble combinations of dyes, or of dyes precipitated upon some inert base.

Some finishing materials are of such a nature that very little is to be gained by analyzing them. Of the mucilages, linseed and Irish moss are prepared by the tanner by extracting the linseed or the moss with hot water. The utmost that can be done toward analyzing such decoctions is to determine the total solids' content of successive batches, to ensure uniformity. Shellac, the proteins, the waxes, and accessory materials, such as formaldehyde, if purchased as the basic raw materials, should be analyzed. Methods for the analysis of these substances are

given below. For the analysis of dry pigments, the reader is referred to any of the standard works on the analysis of pigments used in paints.

Many tanners purchase their finishes already prepared and often combine several such finishes to get the exact effect desired. The analysis of such finishes must be given in outline only, since the number of possible combinations is so great that the analyst is compelled to work out his own methods for the particular mixtures that he happens to encounter.

CASEIN (9)

Commercial casein is prepared by several different processes, and its composition and properties vary with the method employed. The purpose of the analysis is to guarantee uniformity in successive shipments, since the methods of dissolving casein for use in finishing must be changed in details to suit the particular kind of casein employed. The determinations of acidity, viscosity, ash, and calcium are the most useful. The viscosity determination may be modified by making it on a solution prepared as nearly as possible like that in which the casein is dissolved for use.

Water.—Weigh accurately about 5 g. into a wide-mouth, glass-stoppered weighing bottle, previously dried at 100°C. and weighed. Place the bottle, with stopper removed, in an oven at 100 to 102°C. overnight. Replace the stopper, cool in a desiccator, and weigh. Repeat to constant weight. Calculate and report percentage of water from the loss in weight.

Ash.—Weigh accurately about 3 g. into a weighed platinum or quartz dish. Heat over a very low flame until the material is completely charred, taking care that the casein does not ignite. Then place the dish in an electric muffle furnace, and complete the ashing at dull red heat. Cool in a desiccator, and weigh. Calculate percentage of ash.

$$\text{Per cent ash} = \frac{\text{g. ash} \times 100}{\text{g. sample}}$$

It has been suggested that, in the case of caseins low in calcium, a known amount of a calcium solution should be added before ashing, in order to retain all the phosphorus. The weight of ash is corrected by subtracting the weight of calcium salt added. The authors prefer to determine ash without the addition of calcium solution and determine phosphates in a separate sample ashed under conditions such that no phosphorus can escape.

Calcium.—Dissolve the ash obtained as described above in hot dilute hydrochloric acid. Filter, wash the filter paper thoroughly with small quantities of hot water, receive the filtrate and washings in a 100-cc. volumetric flask, and make up to the mark. Pipette 50 cc. into a beaker, add 1 cc. of concentrated sulfuric acid, and heat to boiling. Add 100 cc. of 95-per cent alcohol, stir well, and let stand overnight. Filter through a weighed Gooch crucible, previously dried at 120°C., wash the precipitate with alcohol until free from acid, dry at 120°C., cool in a desiccator, and weigh. Calculate and report percentage of calcium as oxide.

$$\text{Per cent CaO} = \frac{\text{g. CaSO}_4 \times 82.4}{\text{g. sample weighed for ash}}$$

Phosphorus.—Weigh accurately about 3 g. of casein into a platinum or quartz dish, moisten the sample with a few cubic centimeters of calcium acetate solution (prepared by dissolving 50 g. of pure calcium carbonate in dilute acetic acid and diluting to 1,000 cc.), and ignite as described under the determination of ash. Treat the ash with about 10 cc. of concentrated nitric acid, and heat on the water bath until solution is complete. Transfer the solution to a small beaker, and heat to boiling. Make the solution slightly alkaline with ammonia, then add nitric acid drop by drop until it is just acid to litmus. Add 2 g. of solid ammonium nitrate. Heat nearly to boiling, and add about 25 cc. of ammonium molybdate solution (see below). Digest for 1 hr. at about 65°C. Add a few drops of ammonium molybdate solution to the clear supernatant solution to make sure that precipitation is complete. Wash by decantation with 5-per cent ammonium nitrate solution, pouring the washings through a filter paper but retaining as much as possible of the precipitate in the beaker. Add to the precipitate just enough concentrated ammonium hydroxide to effect complete solution, dilute with 4 volumes of water, and pour the solution through the filter. Wash the beaker and filter with hot water, keeping the total volume of the filtrate under 100 cc. Add concentrated hydrochloric acid drop by drop until the solution is faintly acid, then make it just alkaline with ammonia. Cool. Add slowly, with constant stirring, about 10 cc. of magnesia mixture, let stand 15 min., then add about 15 cc. of concentrated ammonium hydroxide. Let the precipitate settle overnight. Filter through an ignited and weighed Gooch crucible, wash with a 2.5-per cent solution of ammonium nitrate until the precipitate is free from chlorides, dry at about 100°C., and ignite at the maximum temperature of a good Meker burner. Cool in a desiccator, and weigh. Calculate and report percentage of phosphorus as pentoxide.

$$\text{Per cent P}_2\text{O} = \frac{\text{g. Mg}_2\text{P}_2\text{O}_7 \times 63.78}{\text{g. sample weighed}}$$

Ammonium Molybdate Solution.—Mix 100 g. of pure molybdic acid with 400 cc. of distilled water, and add 80 cc. of concentrated ammonium hydroxide. Let stand until solution is complete. Pour the solution slowly, with stirring, into a mixture of 400 cc. of concentrated nitric acid (sp. gr. 1.42) and 600 cc. of distilled water. The nitric acid must not be poured into the ammonium molybdate. Dissolve 0.05 g. of sodium ammonium hydrogen

phosphate in a little water, and add it to the ammonium molybdate solution to effect clarification. Stir the solution well, then let stand for 24 hr., and decant the clear solution through a filter paper into a large reagent bottle.

Sulfates.—Weigh accurately about 2 g., and mix thoroughly with about 20 g. of pure, anhydrous sodium carbonate in a platinum dish. Cover the mixture with a layer of pure sodium carbonate about 3 mm. thick. Heat the dish in an electric muffle furnace until all organic matter is consumed, taking care that the temperature does not exceed dull red heat. Cool, dissolve the mass in hot water, filter if necessary, transfer the solution to a 300-cc. volumetric flask, and make up to the mark. Pipette 150 cc. into a beaker, acidify with hydrochloric acid, add a few cubic centimeters of bromine water, heat to boiling, and boil till the excess bromine is expelled. Precipitate sulfate as barium sulfate, filter, ignite, and weigh by the usual methods. Calculate and report percentage of sulfate as sulfur trioxide.

Chloride.—Determine chloride in 100 cc. of the solution prepared for the determination of sulfate, either by the Mohr method described under analysis of vegetable tanning materials in Chap. IX or by the Vollhardt method described under analysis of lime liquors in Chap. VIII. Calculate and report percentage of chlorides as chlorine.

Nitrogen.—Weigh accurately about 0.5 g. into a Kjeldahl flask, and determine nitrogen by the Kjeldahl-Gunning method described under analysis of leather in Chap. II. Calculate percentage of nitrogen. If desired, this may be calculated to percentage of casein by multiplying by the factor 6.38.

$$\text{Per cent : } = \frac{\text{cc. 0.1-N H}_2\text{SO}_4 \times 0.14}{\text{g. sample weighed}}$$

$$\text{Per cent casein} = \text{per cent N} \times 6.38$$

Fat.—Grind about 10 to 12 g. of casein until the entire sample passes a sieve of 200 meshes per linear inch. Weigh accurately about 5 g. into an extraction thimble, and extract with chloroform in a Soxhlett apparatus for about 8 hr. Filter the chloroform solution through rapid, dry filter paper, wash out the flask with 3 successive portions of 5 to 10 cc. of chloroform, and receive the filtered solution in a weighed glass dish. Evaporate the chloroform at room temperature; then dry the dish in an oven at 100 to 102°C. for exactly 30 min. Cool in a desiccator for 15 min., and weigh. Calculate and report percentage of fat.

$$\text{Per cent fat} = \frac{\text{g. fat} \times 100}{\text{sample}}$$

Acidity.—The acidity of a specimen of casein is a measure of the amount of alkali required to dissolve it and is of considerable importance in making a casein finish.

Weigh accurately about 1 g. of casein into a 250-cc. glass-stoppered flask or bottle. Add 25 cc. of tenth-normal sodium hydroxide, agitating gently during the addition of the alkali. Stopper, and shake until solution is complete. Wash down the stopper and sides of the bottle with a wash-bottle stream, add 100 cc. of water (neutral to phenolphthalein), add a few

drops of phenolphthalein indicator, and titrate the excess alkali with tenth-normal sulfuric acid, until the pink color disappears. Calculate and report acidity in cubic centimeters of tenth-normal sodium hydroxide per gram of casein.

Acidity (25 - cc. 0.1-N H_2SO_4)
g. sample

Viscosity.—The determination of viscosity is useful in detecting differences between successive shipments of casein, and the viscosity of a casein solution is of importance in itself in affecting the behavior of the finish when applied to leather. If desired, the determination may be carried out on a solution prepared just like that in which the casein is to be used.

Weigh an amount of casein equivalent to exactly 25 g. of dry casein. Mix in a 400-cc. beaker with about 50 cc. of cold water, stir to a thin paste, and let stand overnight. Next day add 25 g. of borax dissolved in 200 cc. of hot water, mix, and heat the solution on a boiling water bath with occasional stirring for at least 6 hr. Transfer the solution to a 250-cc. volumetric flask, cool to 25°C., and dilute to the mark with water. Mix thoroughly. Filter through coarse muslin, to remove solid particles. Determine viscosity of the filtered solution at 25°C. by the Dudley pipette method described under analysis of oils in Chap. XI. Report.

"Viscosity of a 10-per cent solution at 25°C. = —sec. (H_2O = — sec.)."

EGG ALBUMIN. BLOOD ALBUMIN

These materials are marketed as horny, translucent flakes, yellowish-white in the case of egg albumin, amber to dark brown in that of blood albumin. The greater part of the material should dissolve in water, and most of the insoluble matter should be precipitated when the solution is brought to pH = 4.8 and boiled. Methods developed in the authors' laboratory for measuring these properties are given under the determinations of soluble matter, soluble albumin, and soluble non-albumin. A high content of soluble non-albumin indicates the presence of considerable amounts of protein degradation products. The average composition of samples of dried albumins analyzed in the authors' laboratories during the past 10 years is given in Table 59.

Preparation of Sample.—Break up the entire sample with a pestle to a coarse powder, mix, and weigh roughly about 40 g. Grind this portion till all of it passes a sieve of 100 meshes per linear inch. Preserve in a well-stoppered bottle.

Moisture. Direct Method.—Weigh accurately about 5 g., and determine water by drying, as described under analysis of casein.

TABLE 59.—AVERAGE COMPOSITION OF DRIED A

Constituent		
Water.....	16.72	11.85
Total solids.....	83.28	88.15
Insoluble matter.....	9.40	8.94
Soluble matter.....	73.88	79.21
Soluble albumin.....	58.28	59.80
Soluble non-albumin.....	15.60	19.41
Total nitrogen.....	11.30	10.94
Ammonium salts as ammonia.....	1.39	0.79
Total sulfur as sulfur trioxide.....	1.45	2.10
Chlorine.....	1.92	5.64
Ash.....	4.95	13.73
Alkalinity as sodium carbonate.....	1.77	3.59
Sodium chloride.....	1.81	5.85
Sodium sulfate.....	0.83	0.56
Iron and aluminum as oxides.....	0.07	0.12
Calcium as oxide.....	0.06	0.57

Indirect Method.—Subtract percentage of total solids, determined as described below, from 100, and report the difference as water.

Total Solids, Insoluble and Soluble Matter.—Weigh accurately about 5 g. of finely ground albumin, and sprinkle the sample over the surface of about 200 cc. of water (to which has been added a few drops of chloroform) in a large casserole. Do not stir, as this causes the albumin to form gelatinous clumps that are very difficult to dissolve. Allow the albumin to stand in contact with the water overnight. Next morning stir thoroughly, let the solution stand for 1 hr., transfer to a 250-cc. volumetric flask, and dilute to the mark.

Pipette exactly 50 cc. of the well-shaken solution into a weighed glass dish, evaporate to dryness in the oven at 100 to 102°C., heat for at least 2 hr. after all liquid has disappeared, and cool for exactly 15 min. in an "individual" desiccator over concentrated sulfuric acid. Weigh rapidly, replace the dish in the oven for 1 hr., desiccate again for 15 min., and reweigh. Repeat to constant weight. Calculate and report percentage of total solids.

$$\text{Per cent total solids} = \frac{\text{g. residue} \times 500}{\text{g. sample weighed}}$$

Mix about 75 cc. of the albumin solution with about 2 g. of kaolin (of a brand approved for tannin analysis), and filter the solution through thin, fluted filter paper, returning the filtrate to the paper until the filtrate is clear. Collect about 55 to 60 cc. of filtrate, and pipette 50 cc. into a weighed glass dish. Dry and weigh as described for total solids. Calculate and report percentage of soluble matter.

$$\text{Per cent soluble matter} = \frac{\text{g. residue} \times 500}{\text{g. sample weighed}}$$

Subtract percentage of soluble matter from percentage of total solids, and report the differences as percentage of insoluble matter.

Soluble Albumin and Non-albumin.—Prepare a solution of pH = 4.8 by adding 4.0 cc. of tenth-normal acetic acid to 146 cc. of water in a 400-cc. beaker (Pyrex). Heat to boiling, and add, drop by drop, from a pipette, exactly 50 cc. of the albumin solution prepared for the determination of total solids. Keep the solution boiling gently during the addition, but do not apply too much heat, as there is danger of frothing. When all the albumin has been added, cool the solution to 20°C., transfer to a 250-cc. volumetric flask, and make up to the mark. Filter about 150 cc. of the well-mixed solution with the aid of kaolin, as described under the determination of soluble matter, pipette 100 cc. of the clear filtrate into a weighed dish, and dry and weigh as described under the determination of total solids. Calculate and report percentage of soluble non-albumin.

$$\text{Per cent soluble non-albumin} = \frac{\text{g. residue} \times 1,250}{\text{g. sample weighed in making up the solution}}$$

Subtract percentage of soluble non-albumin from percentage of soluble matter, and report the difference as percentage of soluble albumin.

NOTE.—The determinations of total solids, soluble matter, and soluble non-albumin should be carried out in triplicate, and the average of determination agreeing within 0.5 per cent should be reported.

Total Nitrogen.—Determine as directed under analysis of casein.

Ammonium Salts.—Weigh accurately about 2 g. of albumin into a Kjeldahl flask. Add about 200 cc. of water and about 100 cc. of pure butanol. Arrange the flask for distillation as described under the determination of nitrogen in leather (Chap. II). Introduce about 5 cc. of strong sodium hydroxide solution through the stopcock funnel, and distill cautiously until about 100 cc. of distillate has been collected. Receive the distillate in a bulb containing 50.0 cc. of tenth-normal sulfuric acid. Titrate the excess acid with tenth-normal sodium hydroxide using methyl red indicator, and calculate percentage of ammonium salts as ammonia.

$$\text{Per cent NH}_3 = \frac{(50.0 - \text{cc. } 0.1\text{-}N \text{ NaOH}) \times 0.17}{\text{g. sample}}$$

Total Sulfur and Total Chlorine.—Determine as directed under analysis of casein, and report as sulfur trioxide and chlorine

Ash.—Weigh accurately about 5 g. into a weighed platinum dish, and heat over a very low flame until all organic matter is carbonized. Extract the mass with hot water, filter through ashless paper, wash the residue several times, return the paper to the dish, and heat until all organic matter is destroyed. Evaporate the solution to a convenient bulk, transfer it to the dish, evaporate to dryness on the water bath, and heat at about 200°C. Cool in a desiccator, and weigh. Calculate and report percentage of ash. The determination should be done in duplicate, and one residue used for the

determination of sulfates and chlorides, and the other for those of sodium carbonate, iron and aluminum, and calcium.

$$\text{Per cent ash} = \frac{\text{g. ash} \times 100}{\text{g. sample weighed}}$$

Analysis of Ash.—Determine sulfates and chlorides in the ash of one sample of albumin as directed under analysis of egg yolk (Chap. XI). Report percentage of sodium sulfate and sodium chloride. Determine sodium carbonate, iron and aluminum, and calcium in the ash of a second portion, as described under the analysis of the ash of vegetable tanning materials (Chap. IX). Report percentage of sodium carbonate, iron and aluminum as oxides, and calcium as oxide.

WAXES

Carnauba wax is the wax most commonly used in finishing leather, because of its hardness and high melting point. Other waxes used in the leather industry are beeswax, Japan wax, candelilla wax, and montan wax. Some of the constants of these waxes are given in Table 60.

TABLE 60.—CONSTANTS OF SOME WAXES

Kind of wax	Specific gravity	Melting point, degree centigrade	Acid value	Saponification value	Iodine value	Unsaponifiable matter, per cent
Carnauba wax...	0.978	80	1	69	5	50
	0.999	90	10	95	14	55
Beeswax.....	0.950	60	17	82	6	
	0.970	70	22	120	13	
Japan wax.....	0.97	42	11	206	8	
	0.98	55	33	238	15	
Candelilla wax...	0.936	65	0.3	35	5	65
	0.998	92	24	104	58	91
Montan wax.....	76	74	16	50
	90				

The complete analysis of a wax is carried out, in general, like that of a fat, as described in Chap. XI. In waxes, the higher alcohols play the same role as glycerol in fats. These higher

alcohols are, in general, insoluble in water and soluble in organic solvents; hence they appear in the analysis as unsaponifiable matter. Waxes are considerably harder to saponify than are fats, and many of the published values for unsaponifiable matter and saponification value are in error. According to Gnamm (4), a solution of sodium ethoxide, prepared by adding metallic sodium to absolute alcohol, is required in determining saponification value. Another method in use is to employ a mixture of alcohol and benzol as solvent. For details of this and other methods of determining the chemical constants of waxes, and the quantitative determination of adulterants, the larger handbooks on the analysis of fats, oils, and waxes should be consulted (1, 4). The determination of physical constants, described below under carnauba wax, is frequently sufficient for the routine examination of waxes to be used in finishing leather.

CARNAUBA WAX

Carnauba wax is marketed in several grades, including No. 1 yellow, No. 2 yellow, No. 2 north country, and No. 3 north country. The higher grades are said sometimes to contain paraffin, which is used in the purification process. Any admixture of paraffin can be detected by the lowered melting point and specific gravity which results. The lower grades contain variable amounts of dirt, which can be determined as matter insoluble in carbon tetrachloride. Average results obtained in the authors' laboratory in the partial analysis of different grades of carnauba wax are given in Table 61.

TABLE 61.—SOME CONSTANTS FOR CARNAUBA WAX

Grade	Yellow		North country	
	No. 1	No. 2	No. 2	No. 3
Specific gravity.....	0.975	0.960	0.989	0.999
Melting point, degrees centigrade.....	82	82	82	82.5
Matter insoluble in carbon tetrachloride..	0.10	0.15	0.75	1.36
Ash.....	0.05	0.06	0.25	0.62

Sampling.—Carnauba wax comes in lumps, of variable size and frequently of variable appearance. The color of lumps from one bag of No. 2 or No. 3 north country wax may vary from light yellow to dark olive green.

Select about a dozen lumps, fairly representative of the different sorts present, reduce these lumps to small fragments, mix, and take about 100 g. for the analytical sample. Grind this sample to pass a sieve of 60 meshes per linear inch.

Matter Insoluble in Carbon Tetrachloride.—Weigh accurately about 2 g. into a weighed aluminum thimble, previously extracted with carbon tetrachloride and dried at 105°C. Extract with carbon tetrachloride in a flask under a coil condenser (Fig. 79, Chap. XI). When extraction is complete, allow the thimble to drain, let the absorbed solvent evaporate in the air, and dry in an oven at 105°C. for 1 hr. Cool in a desiccator, and weigh. Calculate and report percentage of matter insoluble in carbon tetrachloride.

$$\text{Per cent CCl}_4 - \text{insoluble} = \frac{\text{g. residue} \times 100}{\text{g. sample weighed}}$$

Ash.—Ignite the thimble containing the matter insoluble in carbon tetrachloride until organic matter is destroyed, cool in a desiccator, and weigh. Calculate and report percentage of ash.

$$\text{Per cent ash} = \frac{\text{g. residue} \times 100}{\text{g. sample weighed}}$$

Melting Point.—Melt about 10 g. of wax in a test tube placed in a boiling water bath. Draw a column of wax into each of 3 capillary tubes. Cool in the ice box for at least 48 hr. Determine melting point as described for fats in Chap. XI.

Specific Gravity (Flotation Method).—Pour some of the clear, melted wax on to a clean metal or porcelain surface so as to form several lozenges about an inch in diameter and a few millimeters thick. Allow these tablets to stand at room temperature for at least 48 hr. Break each tablet into small fragments, and select three that are approximately rectangular and that show no sign of air holes. Wet each fragment by brushing with a camel's-hair brush. Drop each fragment in turn into water at 15°C. See that no air bubbles are adhering to the fragment. In general, the fragment will float. Add alcohol a few drops at a time, stirring after each addition, and maintaining the temperature at 15°C., until the fragment neither floats nor sinks, showing that its specific gravity equals that of the solution. Determine the specific gravity of the solution with a pycnometer or by means of the Westphal balance, as described in Chap. XI, and report as the specific gravity of the wax. In case the fragment has a higher specific gravity than water (*i.e.*, sinks in pure water), add strong sodium chloride solution instead of alcohol.

SHELLAC

Shellac is sold in many grades, of which bleached refined, bleached (regular), and orange (A, B, C, and D) are used in leather finishing. The specifications of the American Society for Testing Materials for these grades are given on p. 440 (3).

STANDARD SPECIFICATIONS FOR SHELLAC

(A. S. T. M., D 207-26 and D 237-27)

	Orange shellac				Bleached shellac	
	Grade A	Grade B	Grade C	Grade D	Regular	Re-fined
Iodine number, maximum....	18.0	18.0	18.0	24.3	10	10
Matter insoluble in hot 95-per cent alcohol, maximum, per cent.....	1.75	2.50	3.00	3.00	1.0	0.2
Moisture and volatile matter, maximum, per cent.....	2.0	2.0	2.0	2.0	5.0	5.0
Matter soluble in water, maximum, per cent.....	0.5	0.5	0.5	0.5	1.0	0.3
Wax, maximum, per cent.	5.5	5.5	5.5	5.5	5.5	0.2
Ash, maximum, per cent.....	1.0	1.0	1.0	1.0	1.0	0.3

The following methods for testing shellac are those of the American Society for Testing Materials (D 29-29T), somewhat abridged.

Matter Insoluble in Hot Alcohol (Continuous Extraction Method Suitable for All Grades of Lac).—Use 95-per cent alcohol (U. S. Internal Revenue Bureau Formula 1 or 30 may be used). Any type of siphon extractor where the siphon is continuously surrounded by vapors of hot alcohol may be used. An apparatus that has been found satisfactory is shown in Fig. 82. An 8-in. glass condenser of the Allihn type (with bulbs), the stem of the condenser being perforated with two holes for suspending the siphon, may be substituted for the metal condenser.

Prepare an extraction cartridge 26 mm. in diameter by 80 mm. in height (Schleicher & Schull No. 603 or the equivalent). Place the cartridge in the extraction apparatus, and extract for 30 min. with boiling 95-per cent alcohol. Dry in an air bath at 105°C., transfer to a glass-stoppered weighing bottle, cool, and weigh. Continue drying to constant weight. A number of cartridges may be prepared and kept in glass-stoppered weighing bottles until wanted.

Weigh 5 g. of the lac¹ in a 200-cc. tall-form beaker, and dissolve in 100 to 120 cc. of boiling 95-per cent alcohol. Immerse the beaker in a hot-water

¹ The condenser shall be able to return all the alcohol volatilized during the vigorous boiling of the contents of the flask, the object being to effect the maximum extraction in the minimum time.

When the determination of the alcohol-insoluble matter in bleached shellac is required, the sample, if in the form of hanks or bars or ground bleached shellac, shall be dried, as the water present dilutes the alcohol to a point where solution may not be complete. It is recommended that in

bath, in order to be certain that all the shellac is dissolved and that the wax is in solution. Bring the alcohol and shellac mixture to a brisk boil, and maintain at or near the boiling point for 30 min. Transfer this solution quickly into the weighed extraction cartridge previously wet with boiling-hot alcohol, putting the cartridge into a carbon filter tube of suitable size supported in a hot water bath (Fig. 83), the outlet tube extending through the bottom of the bath allowing the escape of the filtrate. Wash all the residue from the beaker into the cartridge with boiling-hot alcohol. Put the cartridge in the extraction apparatus, and extract to constant weight (in no case less than 1 hr.). Keep the alcohol boiling briskly, and maintain a free flow of cooling water through the condenser during the extraction. The rate of extraction may be controlled by the use of an electric stove, 6-in. in diameter, using a current of 2.2 amp. at 110 volts. Use a volume of 125 cc. of alcohol in the flask, and protect the flask from draughts. Under these conditions the tube shall siphon over at least 33 times in 1 hr.

Iodine Value (Wijs Method).—Prepare a solution of iodine monochloride in glacial acetic acid. The acid must have a melting point of 14.8°C . and be free from reducing impurities. Determine melting point with the apparatus and procedure described under determination of titer test of fatty acids (Chap. XI). Cool the acid to 10°C . in ice water, then stir vigorously, read the thermometer every 15 sec., and take the true melting point as that temperature at which the reading remains constant for at least 2 min. To test for reducing impurities, dilute 2 cc. of the acid with 10 cc. of distilled water, add 0.1 cc. of tenth-normal potassium permanganate solution, and maintain at a temperature of $24^{\circ}\text{C} \pm 3^{\circ}\text{C}$. At the end of 2 hr. the pink color shall not be discharged.

Wijs Iodine Monochloride Solution.—Dissolve 13 g. of iodine in 1 l. of the acetic acid, using gentle heat if necessary, determining the strength by titration with thiosulfate. Set aside 50 to 100 cc. of the solution, and introduce dry chlorine gas into the remainder until the characteristic color change occurs and the halogen content has been nearly doubled, as ascer-

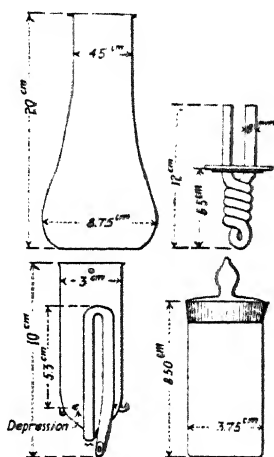


FIG. 82.—Extraction apparatus for alcohol-insoluble matter in shellac.

preparing shellac for this determination, a separate portion be dried by exposure to the air in a thin layer, without the application of heat.

Occasionally, shellacs, including dry bleached shellac, are met with that will not give the usual 33 siphons per hour. These shellacs should be reported as abnormal. This condition can usually be overcome by using a smaller quantity (2 g.) of shellac for the determination and proceeding as described above.

by titration. If the halogen content has been more than doubled, reduce it by adding the requisite quantity of the iodine-acetic acid solution.

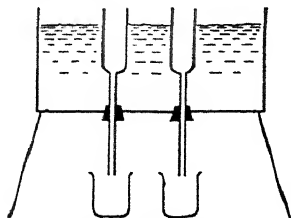


FIG. 83.—Filtering device.

A slight excess of iodine does no harm, but an excess of chlorine shall be avoided.

NOTE. *Example:* If the titration of 20 cc. of original iodine-acetic acid solution required 22 cc. of tenth-normal thiosulfate, 20 cc. of the finished Wijs solution should require between 43 and 44 cc. of the thiosulfate solution.

The Wijs solution should be tested against an orange shellac the iodine number of which is accurately known. The iodine number thus obtained should be

within ± 0.5 of the known iodine number.

Determination.—Introduce a 0.2-g. sample¹ of finely ground shellac into a 250-cc. dry, clear glass bottle having a ground-glass stopper. Add 20 cc. of glacial acetic acid, and twirl the bottle gently on top of a hot water bath at 65 to 70°C., until solution is complete, except for the wax. This should not require more than 15 min. A pure shellac is rather difficultly soluble; solution is quicker according to the percentage of rosin present. Add 10 cc. of chloroform, and cool the solution to from 21.5 to 22.5°C. Allow the bottle to stand for at least 30 min. half immersed in a shallow pan of water at a temperature of 21.5 to 22.5°C., well insulated or equipped with a suitable thermostat, before adding the Wijs solution. Add 20 cc. of the Wijs solution,¹ which shall be at a temperature of 21.5 to 22.5°C., from a pipette having a rather small delivery aperture (about 30 sec.). Close the bottle, place it again into the pan of water, and note the time. The bottle shall be kept half immersed in water at from 21.5 to 22.5°C. during the 1 hr. that the shellac is exposed to the Wijs solution. Twirl the bottle occasionally during the hour. After exactly 1 hr., add 10 cc. of freshly prepared potassium iodide solution, washing into the bottle any Wijs solution on the stopper with the same. Titrate the solution immediately with about 25 to 30 cc. of tenth-normal sodium thiosulfate solution, allow the solution to run in rapidly, and shake vigorously until it becomes a straw color. Now add 15 cc. of freshly prepared starch solution, and slowly finish titrating. The end point is sharp; disregard any color returning after about 30 sec.

¹ In the case of grossly adulterated samples, or in the testing of pure rosin, it is necessary to use, instead of 0.2 g. of material, a smaller quantity (0.15 or 0.1 g.) in order that the excess of iodine monochloride may not be too greatly reduced, since the excess of halogen is one of the factors in determining the amount of absorption. In case less than 25 cc. of the thiosulfate solution is required, another test shall be made, using a smaller quantity of the shellac.

In weighing shellac, some difficulty is at times experienced on account of its electrical properties. In very dry weather it may be found that the necessary handling to prepare it for weighing has electrified it and that

Run a blank determination on the reagents at the same time. The blank is necessary on account of the well-known effect of temperature changes on the volume and possible loss of strength of the Wijs solution.

A determination on a sample of pure shellac of known iodine value shall also be run with every set of tests.

Qualitative Test for Rosin.—Add 20 cc. of absolute alcohol or glacial acetic acid (melting point 13 to 15°C.) to 2 g. of the shellac, and thoroughly dissolve. Add 100 cc. of petroleum ether, and mix thoroughly. Add approximately 2 l. of water, and separate a portion of the ether layer (at least 50 cc.), and filter if cloudy. Evaporate the petroleum ether, and test the residue with the Halphen-Hicks reagent as follows:

Solution A.—One part by volume of phenol dissolved in two parts by volume of carbon tetrachloride.

Solution B.—One part by volume of bromine dissolved in four parts by volume of carbon tetrachloride.

Add 1 to 2 cc. of solution A to the residue left after evaporation of the petroleum ether solution, and pour this mixture into a cavity of an ordinary porcelain color-reaction plate until it just fills the depression. Immediately fill an adjacent cavity with solution B. Cover the plate with an inverted watch glass, and note the color, if any, produced in the former solution by the action of the bromine vapors from solution B. A decided purple or deep indigo blue color is an indication of the presence of rosin.

Qualitative Test for Copal.—Make approximately a 35-per cent solution of the shellac in 95-per cent denatured alcohol, then filter. To 10 cc. of this filtrate in a large test tube (6 by $\frac{3}{4}$ in.) add 99-per cent methyl alcohol nearly to fill the tube, and thoroughly mix. The formation of a precipitate after standing is an indication of copal. Shellac free from copal should remain clear.

Since the variation between the highest and lowest iodine numbers of a pure shellac is not great, it is recommended that the following assumptions be made:

Assumed iodine number of	
Rosin-free and copal-free orange shellac	18
Rosin-free and copal-free bleached shellac	10
Rosin	228
Copal	130

The percentages of adulterants shall be determined from the following equations:

it may be necessary to leave it in the balance pan at rest for a few minutes before determining the weight.

If a number of samples are being run, at least 5 min. shall be allowed between the additions of the Wijs solution.

From the difference between the blank titration and the titration of the sample and the iodine value of the sodium thiosulfate solution, calculate the iodine number of the sample tested. (Iodine number is given in centigrams of iodine to 1 g. of sample.)

$$\text{Percentage of rosin in orange shellac} = x - 18$$

$$\text{Percentage of rosin in bleached shellac} = \frac{x - 10}{228 - 10} \times 100$$

$$\text{Percentage of copal in orange shellac} = \frac{x - 18}{130 - 18} \times 100$$

$$\text{Per centage of copal in bleached shellac} =$$

where

x = the iodine number of the sample under test, determined as described above.

NOTE.—The results obtained by assuming the values of 18 and 10 as the iodine number of orange and bleached shellac, respectively, and 228 as the iodine number of rosin may give a slightly lower percentage of rosin, under some circumstances, than that which is actually present.

Moisture. *a. Orange Shellac and Dry-bleached Shellac.*—Weigh a sample of 5 g. in a flat-bottomed dish about 4 in. in diameter, and place the dish in a well-ventilated gas or electric oven for at least 6 hr. at 41°C. + 2°C., cool in a desiccator, and weigh. Continue heating to constant weight.

NOTE.—Dry-bleached shellac is also termed “bone dry,” “kiln-dry,” or “vac-dry” bleached shellac.

b. Hanks and Ground-bleached Shellac.—Weigh a 5-g. sample in a flat-bottomed dish about 4 in. in diameter, and dry in a desiccator over sulfuric acid for at least 12 hr. Place the dish in a well-ventilated gas or electric oven for at least 6 hr. at 41°C. ± 2°C., cool in a desiccator, and weigh. Continue heating to constant weight.

NOTE.—Average commercial orange shellac contains not more than 2 per cent of moisture.

Average commercial regular dry-bleached and dry-refined bleached shellac contain not more than 6 per cent of moisture.

Average commercial regular and refined bleached shellac in the form of hanks or bars, or ground bleached, contain not more than 25 per cent of moisture.

Wax.—The 95-per cent alcohol may be U. S. Internal Revenue Bureau Formula 1 or 30. The chloroform or carbon tetrachloride must be redistilled. The filter cell must be extracted with either chloroform or carbon tetrachloride.

Average commercial orange or dry-bleached shellac contains about 4 to 5.5 per cent of wax; dry-bleached refined shellac is practically free from wax. The procedure used in determining wax is different for the two kinds of materials. For the procedure for “machine-made” and “garnet” lacs, the original publications of the American Society for Testing Materials should be consulted.

a. Orange, Button, Seed, and Regular Bleached Shellac.—Dissolve 10 g. of finely ground dry shellac¹ in 200 cc. of alcohol at a temperature of $24^{\circ}\text{C}.$ $\pm 1^{\circ}\text{C}.$ Allow the solution to stand for several hours (preferably overnight) in a tall-form covered beaker, maintained at a temperature of $24^{\circ}\text{C}.$ $\pm 1^{\circ}\text{C}.$, until the wax has settled to a small layer at the bottom. Decant the clear solution through a 12.5-cm. folded filter paper, taking care not to disturb the wax layer.¹ Finally, wash the wax on to the filter paper, using approximately 25 cc. of alcohol at the prescribed temperature. Wash the beaker and the wax with three 25-cc. portions of the alcohol by directing a fine stream of alcohol from a wash bottle on to the edge of the filter paper, as the shellac has a tendency to dry on the edge. The final washings should be colorless, and the total filtrate should not exceed 300 cc. Allow most of the alcohol to evaporate from the filter paper at a temperature of $43^{\circ}\text{C}.$; when dry, wrap in a clean filter paper ($4\frac{1}{2}$ by $4\frac{1}{2}$ in.), and place in a Soxhlet siphon or any suitable continuous extraction apparatus.¹ Remove any wax from the beaker by boiling with approximately 50 cc. of chloroform, and filter this into the thimble. Extract for at least 1 hr., then distill off most of the chloroform, and complete the evaporation on a water bath. Dry the wax residue at $105^{\circ}\text{C}.$ to within 10 mg. of constant weight.

b. Dry-bleached Refined Shellac.—In the case of dry-bleached refined shellac, dissolve 50 g. in 250 cc. of alcohol, add 1 g. of oxalic acid, and stir until all is dissolved. Then add 0.5 g. of filter cell, and allow to settle overnight. Run the clear solution through a Gooch crucible prepared with asbestos. Wash the sediment of wax and filter cell on to the crucible with alcohol. Dry at a low temperature, remove the asbestos mat, wrap in filter paper, and extract in continuous extraction apparatus with chloroform or carbon tetrachloride for 1 hr. Dry the wax at $105^{\circ}\text{C}.$ to constant weight.

Matter Soluble in Water.—Weigh 10 to 25 g. of the finely ground sample accurately, and stir thoroughly with 200 cc. of distilled water in a suitable-size flask or beaker. Cover with a watch glass, and allow to stand at room temperature (approximately $21^{\circ}\text{C}.$) for 4 hr., stirring occasionally. Decant the water through a 12.5-cm. filter paper into a weighed evaporating dish, washing the shellac and filter paper with at least 100 cc. of water. Evaporate the water, and dry the extract at 105 to $110^{\circ}\text{C}.$ for 1 hr. or more to

¹ When the wax determination is made on bleached shellac in the form of hanks or bars or ground bleached shellac, the sample shall be dried as the water present dilutes the alcohol to a point where solution may not be complete. It is recommended that in preparing shellac for this determination, a separate portion be dried by exposure to the air in a thin layer, without the application of heat.

Shellac wax is not strictly insoluble in alcohol, the solubility increasing with a rise in temperature, but the above method gives results sufficiently accurate for commercial purposes providing the temperature is maintained within the prescribed limits.

During the filtration the funnel should be covered with a watch glass to prevent evaporation of alcohol and drying of shellac on the edge of the paper.

It is recommended that the wrapped wax residue be placed in a Schleicher & Schull or similar type extraction thimble or cartridge, 25 by 70 mm., to prevent any insoluble matter being carried over.

constant weight. Cool, weigh, and calculate the percentage of matter soluble in water.

Ash.—Char a weighed quantity (3 to 5 g.) of the shellac, and ignite at a low heat, not exceeding dull redness, until free from carbon. If a carbon-free ash cannot be obtained in this manner, exhaust the charred mass with hot water, collect the insoluble residue on an ashless filter, and burn the filter and contents until all the carbon is consumed. Add the filtrate, evaporate to dryness, and heat to dull redness. Cool in a desiccator and weigh.

Color.—Digest a weighed portion of the shellac with twice its weight of cold 95-per cent alcohol, shaking at intervals until the shellac is entirely "cut." Then compare the color with that of a standard sample, either by comparing the solutions in clear glass tubes or by comparing films spread on porcelain plates.

GUMS AND MUCILAGES

The gums used in leather finishes include gum arabic, gum tragacanth, gum tragasol, dextrin, Irish moss, linseed, algin, isinglass, etc. In testing such materials, the most useful determinations include matter soluble in water, ash, viscosity and pH values of standard solutions, and specific qualitative tests serving to identify the particular material or to identify adulterants. The latter are most important in the cases of gum Arabic and gum tragacanth, which are sometimes adulterated with starch or dextrin. For details, consult the larger handbooks on organic analysis (1).

FORMALDEHYDE (1)

Formaldehyde is used in the preparation of finishes, as a disinfectant, and as a reducing agent. Its use has been proposed for tanning. Commercial formaldehyde, or formalin, is a 40-per cent aqueous solution. The solution should contain not more than 0.2 per cent acid as formic acid.

Specific Gravity.—Determine with the pycnometer, as directed under the analysis of formic acid.

Non-volatile Matter.—Pipette 10 cc. into a weighed platinum dish, and evaporate to dryness on the hot bath under a hood. Cool in a desiccator, and weigh. Calculate and report percentage of non-volatile matter.

$$\text{Per cent non-volatile matter} = \frac{\text{due} \times 1}{\text{sp. gr. of sample}}$$

Ash.—Ignite the non-volatile residue at dull red heat, cool in a desiccator, and weigh. Calculate and report percentage of ash. If appreciable quantities are present, analyze the ash for the metals as directed under ash of vegetable-tanned leather (Chap. II).

Total Acid as Formic Acid.—Weigh accurately about 10 g., and dissolve in exactly 1,000 cc. Pipette 100 cc. of this solution into an Erlenmeyer

flask, add a few drops of phenolphthalein indicator, and titrate with tenth-normal sodium hydroxide to the appearance of a faint pink color. and report percentage of total acid as formic acid.

$$\text{Per cent HCOOH} = \frac{\text{cc. 0.1-N NaOH} \times 4.6}{\text{g. sample weighed}}$$

Formaldehyde.—Measure exactly 50 cc. of normal sodium hydroxide into a 500-cc. Erlenmeyer flask. Add 50 cc. of pure hydrogen peroxide (3-per cent solution), previously rendered exactly neutral to phenolphthalein. Weigh accurately a small glass-stoppered weighing bottle, introduce about 3 cc. of formaldehyde, stopper, and reweigh. Rinse the sample from the weighing bottle to the alkaline peroxide solution, using the minimum quantity of water. Place a short-stemmed funnel in the mouth of the flask, and boil for 5 min. Cool, rinse down the funnel and sides of the flask, and titrate the excess sodium hydroxide with normal sulfuric acid. Calculate and report percentage of formaldehyde.

In this procedure, formaldehyde is oxidized to formic acid, which neutralizes part of the alkali present. A correction must be made for formic acid present initially.

$$\text{Per cent HCHO} = \frac{(\text{50} - \text{cc. 1-N H}_2\text{SO}_4) \times 3}{\text{g. sample weighed}} - (\text{per cent HCOOH} \times 0.652)$$

PIGMENT FINISHES

Total Solids.—Weigh rapidly about 5 g. of the *well-mixed* pigment into a porcelain dish, dry in an oven at about 105°C., cool in a desiccator, and weigh. Calculate and report percentage of total solids.

This determination is useful in detecting differences between successive shipments of the same pigment finish. Obviously, if different shipments contain widely differing quantities of pigment in a given volume, the results obtained when a constant quantity of each is employed in a blended finish will be erratic.

Mineral Matter.—Ignite the residue obtained in determining total solids, cool in a desiccator, and weigh. Calculate percentage of mineral matter.

This determination tells, in the first place, whether an inorganic pigment or an organic lake has been employed. In the former case, qualitative tests may be performed to determine the nature of the pigment, when this is not obvious from its appearance.

Proteins.—In the absence of lakes, or appreciable quantities of dyes, determine nitrogen by the Kjeldahl method, as described in Chap. II. In considerable amounts of dyes are present, perform qualitative tests for the commoner proteins, such as casein, albumin, and gelatin, consulting the larger works on organic analysis (1).

The presence of proteins in a pigment finish generally can be established from the odor of putrefaction that develops when the finish is allowed to stand for a few days exposed to the air.

Shellac.—Dry enough of the finish to give about 10 g. of residue, reduce the residue to a powder, and extract 5 g. with alcohol in a Soxhlett apparatus. Evaporate the alcohol, and weigh the residue. Repeat until no more material is extracted. If the material extracted by alcohol has the characteristic physical properties of shellac, take the percentage extractable by alcohol as the approximate percentage of shellac in the pigment finish.

Wax.—After extracting the solid matter with alcohol, as described above, repeat the extraction using carbon tetrachloride. Evaporate the solvent, and weigh the residue. If the residue has the characteristic physical properties, including melting point, of one of the commoner waxes, take the percentage extractable by carbon tetrachloride as the approximate percentage of wax in the pigment finish.

LINSEED OIL (3)

Linseed oil is the most important material used in making ordinary patent leather. The following methods for its analysis are those of the American Society for Testing Materials (Standard Specifications for Raw Linseed Oil: D 234-28, and Tentative Specifications for Boiled Linseed Oil: D 260-28 T). Unless otherwise stated, the methods given apply both to the raw and to boiled oil.

PROPERTIES AND TESTS

Linseed oil shall be the pure oil pressed from flaxseed and shall conform to the following requirements:

	Maximum	Minimum
Specific gravity at $\frac{15.5}{15.5}^{\circ}\text{C} \dots$	0.936	0.931
Acid number.....	4.0	
Saponification number.....	195.0	189.0
Unsaponifiable matter, per cent.....	1.50	
Iodine number (Wijs)*.....	177.0
Loss on heating at 105 to $110^{\circ}\text{C}.$, per cent.....	0.2	
Color.....	Not darker than a freshly prepared solution of 1.0 g. potassium bichromate in 100 cc. of pure sulfuric acid (sp. gr. 1.84)	
Foots, per cent:		
Heated oil....	1.0	
Chilled oil....	4.0	

* If linseed oil of the high-iodine-number type is desired, the minimum iodine number, as specified above, should be changed to 188.0

Boiled linseed oil shall be pure linseed oil that has been treated by heating and incorporating compounds of lead and, at the option of the manufacturer, suitable compounds of other drying metals, so as to produce a product that will dry rapidly. It shall be clear, free from sediment, and shall conform to the following requirements, when tested in accordance with the methods described below:

	Maximum	Minimum
Time of drying on glass, hours.....	18.0	
Specific gravity at $\frac{15.5}{15.5}$ °.....	0.945	0.931*
Acid number.....	7.5	
Saponification number.....	195.0	189.0
Unsaponifiable matter, per cent.....	1.50	
Iodine number (Wijs).....		170.0
Loss on heating at 105 to 110°C., per cent.....	0.2	
Ash, per cent.....	0.50	
Lead, per cent.....		0.05

* When a high-viscosity type of boiled linseed oil is required, the specific gravity shall not be less than 0.937.

METHODS OF TESTING

Solutions Required

The following reagents will be required:

a. Standard Sodium Hydroxide Solution.—Prepare a stock concentrated solution of sodium hydroxide by dissolving sodium hydroxide in water in the proportion of 200 g. of sodium hydroxide to 200 cc. of water. Allow this solution to cool and settle in a stoppered bottle for several days. Decant the clear liquid from the precipitate of sodium carbonate into another clean bottle. Add clear barium hydroxide solution until no further precipitate forms. Again allow to settle until clear. Draw off about 175 cc., and dilute to 10 l. with freshly boiled distilled water. Preserve in a stock bottle provided with a large guard tube filled with soda lime. Determine the exact strength by titrating against pure benzoic acid, C_6H_5COOH , using phenolphthalein as indicator.¹ This solution will be approximately fourth-normal, but do not attempt to adjust it to any exact value. Determine its exact strength, and make proper corrections in using it.

b. Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95-per cent ethyl alcohol in the proportion of about 22 g. per 1,000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used; it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g. to 1,000 cc.), kept

¹ See *U. S. Bur. Standards Sci. Paper* 183.

at about 50°C. for 15 days, and then distilled. For an alternate method see *Journal American Chemical Society*.¹

c. **Half-normal Sulfuric Acid Solution.**—Add about 15 cc. of sulfuric acid (sp. gr. 1.84) to distilled water, cool, and dilute to 1,000 cc. Determine the exact strength by titrating against freshly standardized NaOH or by any other accurate method. Either adjust to exactly half-normal strength or leave as originally made, applying appropriate correction.

d. **Wijs Iodine Monochloride Solution.**—Prepare as directed under analysis of shellac.

e. **Starch Solution.**—Stir up 2 to 3 g. of potato starch or 5 g. of soluble starch with 100 cc. of 1-per cent salicylic acid solution, add 300 to 400 cc. of boiling water, and boil the mixture until the starch is practically dissolved. Dilute to 1 l

f. **Potassium Iodide Solution (15-Per Cent).**—Dissolve 150 g. of potassium iodide free from iodate in distilled water, and dilute to 1,000 cc.

g. **Standard Sodium Thiosulfate Solution.**—Dissolve pure sodium thiosulfate in distilled water that has been well boiled to free it from carbon dioxide in the proportion so that 24.83 g. of crystallized sodium thiosulfate will be present in 1,000 cc. of the solution. It is best to let this solution stand for about 2 weeks before standardizing. Standardize with pure resublimed iodine.² This solution will be approximately tenth-normal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly tenth-normal strength. Preserve in a stock bottle with a guard tube filled with soda lime.

h. **Acid Calcium Chloride Solution.**—Saturate with calcium chloride a mixture of 90 parts of water and 10 parts of hydrochloric acid (sp. gr. 1.19).

Methods

Applicable to Raw and to Boiled Oil

The oil shall be tested in accordance with the following methods, and all tests shall be made on oil which has been thoroughly agitated before the removal of a portion for analysis:

a. **Specific Gravity.**—Use a pycnometer, accurately standardized and having a capacity of at least 25 cc., or any other equally accurate method, making the test at 15.5°C., water being 1.000 at 15.5°C.

b. **Acid Number.**—Weigh from 5 to 10 g. of the oil. Transfer to a 300-cc. Erlenmeyer flask. Add 50 cc. of a mixture of equal parts by volume of 95-per cent ethyl alcohol and chemically pure reagent benzol. (This mixture should be previously titrated to a very faint pink with dilute alkali solution, using phenolphthalein as an indicator.) Add phenolphthalein indicator, and titrate at once to a faint permanent pink color with fifth-normal sodium hydroxide solution. Calculate the acid number (milligrams of potassium hydroxide per gram of oil).

¹ P. 395, 1906.

² See TREADWELL-HALL, "Analytical Chemistry," 3d ed., vol. II, p. 646, John Wiley and Sons, Inc., New York.

c. Saponification Number.—Weigh about 2 g. of the oil in a Erlenmeyer flask. Add 25 cc. of alcoholic sodium hydroxide or potassium hydroxide solution. Put a condenser loop inside the neck of the flask, and heat on the steam bath for 1 hr. Cool, add phenolphthalein as indicator, and titrate with half-normal sulfuric acid. Run two blanks with the alcoholic sodium hydroxide solution. These should check within 0.1 cc. of half-normal sulfuric acid. From the difference between the number of cubic centimeters of half-normal sulfuric acid required for the blank and the number required for the determination, calculate the saponification number (milligrams of potassium hydroxide required for 1 g. of the oil).

d. Unsaponifiable Matter.—Weigh 8 to 10 g. of the oil. Transfer to a 250-cc. long-neck flask. Add 5 cc. of a strong solution of sodium hydroxide (equal weights of sodium hydroxide and water) and 50 cc. of 95-per cent ethyl alcohol. Put a condenser loop inside the neck of the flask, and boil for 2 hr. Occasionally agitate the flask to break up the liquid, but do not project the liquid on to the sides of the flask. At the end of 2 hr., remove the condenser and allow the liquid to boil down to about 25 cc.

Transfer to a 500-cc. glass-stoppered separatory funnel, rinsing with water. Dilute with water to 250 cc., and add 100 cc. of redistilled ether. Stopper, and shake for 1 min. Let stand until the two layers separate sharp and clear. Draw all but 1 or 2 drops of the aqueous layer into a second 500-cc. separatory funnel, and repeat the process using 60 cc. of ether. After thorough separation, draw off the aqueous solution into a 400-cc. beaker, then the ether solution into the first separatory funnel, rinsing down with a little water. Return the aqueous solution to the second separatory funnel, and shake out again with 60 cc. of ether in a similar manner, finally drawing the aqueous solution into the beaker and rinsing the ether into the first separatory funnel.

Shake the combined ether solution with the combined water rinsings, and let the layers separate sharp and clear. Draw off the water, and add it to the main aqueous solution. Shake the ether solution with two portions of water (about 25 cc. each). Add these to the main water solution.

Swirl the separatory funnel so as to bring the last drops of water down to the stopcock, and draw off until the ether solution just fills the bore of the stopcock. Wipe out the stem of the separatory funnel with a bit of cotton on a wire. Draw the ether solution (portionwise if necessary) into a 250-cc. flask, and distill off. While still hot, drain the flask into a small weighed beaker, rinsing with a little ether. Evaporate this ether, cool the beaker, and weigh. (The unsaponifiable oil from adulterated drying oils may be volatile and as a consequence may evaporate on long heating. Therefore, heat the beaker on a warm plate, occasionally blowing out with a current of dry air. Discontinue heating as soon as the odor of ether is gone.)

e. Iodine number.—Place a small quantity of the sample in a small weighing burette or beaker. Weigh accurately. Transfer by dropping from 0.09 to 0.15 g. of oil to a 500-cc. bottle, having a well-ground glass stopper; or an Erlenmeyer flask, having a specially flanged neck for the iodine tests. Reweigh the burette or beaker, and determine the amount of sample used. Add 10 cc. of chloroform. Whirl the bottle to dissolve the sample.

Add 10 cc. of chloroform to each of two empty bottles like that used for the sample. Add to each bottle 25 cc. of the Wijs solution, and let stand with occasional shaking for 1 hr. in a dark place at a temperature of from 21 to 23°C. Add 10 cc. of the potassium iodide solution (15-per cent) and 100 cc. of water. Titrate with tenth-normal sodium thiosulfate, using starch as an indicator. The titrations on the two blanks tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the samples and the iodine value of the thio-sulfate solution calculate the iodine number of the samples tested. (Iodine number is given in centigrams of iodine to 1 g. of sample.)

f. Loss on Heating at 105 to 110°C.—Place 10 g. of the oil in an accurately weighed 50-cc. Erlenmeyer flask, and weigh. Heat in an oven at a temperature between 105 and 110°C. for 30 min., then cool and weigh. Calculate the percentage of loss. This determination shall be made in a current of carbon dioxide gas.

(Applicable to Raw Oil Only)

g. Color.—Prepare a fresh solution of 1 g. of pure potassium bichromate in 100 cc. of pure concentrated colorless sulfuric acid (sp. gr. 1.84). Place the oil and colored concentrated solution in separate thin-walled clear-glass tubes of the same diameter (1 to 2 cm.) to a depth of not less than 2.5 cm., and compare the depths of color by looking transversely through the columns of liquid by transmitted light.

h. Determination of Percentage of Foots (Method).—With all materials at a temperature between 20 and 27°C., mix, by shaking for exactly 1 min. in a graduated tube, 25 cc. of the well-shaken sample of oil, 25 cc. of acetone and 10 cc. of the acid calcium chloride solution. The tube shall then be clamped in an upright position where settling can take place for 24 hr. The temperature during this period should be between 20 and 27°C.

The volume of the stratum lying between the clear calcium chloride solution and the clear acetone and oil mixture is read in 0.1 cc. or a fraction thereof. This reading multiplied by 4 expresses the amount of foots present as a percentage by volume.

The tube referred to may be a burette or a color-comparison tube. It should have an internal diameter of 1.0 to 1.5 cm. and a capacity of not less than 70 cc. The graduations in 0.1 cc. should extend at least from 10 to 50 cc. above the bottom of the tube. The acid calcium chloride solution is prepared by saturating with calcium chloride a mixture of 90 parts water and 10 parts concentrated hydrochloric acid (sp. gr. 1.19).

Heated Oil Test.—Heat a portion of the oil to 65°C., hold it within 2°C. of that temperature for 10 min., then cool it to room temperature (20 to 27°C.). Subject the sample promptly to the foots test as described above.

Chilled Oil Test.—Heat a portion to 65°C., hold it within 2°C. of that temperature for 10 min., then place it in a dry clean bottle, stopper tightly, and place in a cracked ice and water mixture (0°C.) for exactly 2 hr. At the end of this time, place the bottle for exactly 30 min. in a water bath at 25°C., then subject promptly to the foots test as described above.

Applicable to Boiled Oil Only

Time of Drying on Glass.—In determining the time of drying on glass, flow the sample over a perfectly clean glass plate. Place the plate in a vertical position in air that is at $30^{\circ}\text{C.} \pm 2^{\circ}\text{C.}$ and of a humidity of 32-per cent ± 4 per cent saturation. After about 2 hr., test the film at intervals with the finger at points not less than 2.5 cm. from the edges. The film shall be considered dry when it no longer adheres to the finger and does not rub up appreciably when the finger is lightly rubbed across the surface.

Ash.—In determining ash, weigh a porcelain crucible or dish. Add from 10 to 25 cc. of the sample, carefully weighing the amount added. Place on a stone slab on the floor of a hood. Ignite by playing the flame of a burner on the surface of the oil, and allow to burn quietly until most of the oil is burned off; then transfer to a muffle or over a flame, and continue heating at a low temperature (not over a dull red) until all carbonaceous matter is consumed. Cool, weigh, and compute percentage of ash.

Lead.—In determining lead, dissolve the ash in dilute nitric acid to which a little hydrogen peroxide has been added, and determine lead by the sulfate or any other equally accurate method.

Appearance.—Transfer a portion of the sample to a clear glass tube, and note appearance.

Control Methods for the Boiling of Linseed Oil.—The control of the boiling of linseed and other drying oils, a process which consists of heating the oil together with one of a number of driers, has until recently been vested almost entirely in skilled workmen, who know by long experience the appearance, consistency, stringiness, etc., which an oil should have at the end of the operation, in order that it shall be satisfactory in use. With increasing knowledge of the chemical changes taking place during boiling, it is becoming possible to follow the process by exact chemical and physical measurements. Long (6) and his associates have shown that the most important change occurring during the heating of linseed oil with driers is polymerization, that is, an increase in the average molecular weight of the oil. Changes in molecular weight can be followed very accurately by changes in the depression of the freezing point of benzene, which occur when the oil is dissolved in this solvent. Long recommends dissolving about 0.8 g. of the oil, weighed accurately, in 25 cc. of benzene. The solvent should be redistilled, thiophene-free benzene, boiling between 80.0 and 80.3°C. For the technique of determining the freezing point and the method of calculating the molecular weight of the oil from the freezing-point lowering, a manual of practical physical chemistry should be consulted. The determinations may be made quickly enough to be used for determining the

proper point to discontinue heating the oil, which is the point at which the molecular weight of the oil has risen to the value previously found to be coincident with a satisfactory product.

VULCANIZED OILS (VISCOLS)

Vulcanized oils are animal or vegetable oils treated with sulfur monochloride. As the proportion of sulfur monochloride to oil is increased, the product becomes more and more viscous and eventually assumes the properties of a gummy or rubbery solid. The properties of the product depend to a large extent upon the kind of oil that is treated. Vulcanized oils are soluble in naphtha, and the product as marketed contains about 40 per cent by weight of this solvent.

In analyzing vulcanized oils, naphtha is determined by loss in weight at 100°C. and also by distillation. The latter method yields results that are lower than the former but enables the analyst to determine the specific gravity of the naphtha incorporated in the oil. The kind of oil employed is found out by determining unsaponifiable matter, unoxidized fatty acids, and oxidized fatty acids, exactly as in the case of ordinary oils; and by determining the iodine value, melting point, and other constants of the unoxidized acids and of the unsaponifiable matter in case appreciable amounts of the latter are present. The constants of the oxidized fatty acids have no particular significance. The percentage of oxidized acids found varies with the kind of oil employed and with the extent of vulcanization. Chlorine and sulfur are determined to find out how far vulcanization has been carried; they should be present in nearly constant relative amounts. Ash should be negligible in amount. Of physical properties, viscosity is highly important, from the point of view of determining the behavior of the material when applied to leather; the viscosity is affected enormously by the naphtha content, and variations of this constituent must be considered in interpreting viscosity values. Specific gravity has no significance except as a check on constancy of composition of successive shipments.

Specific Gravity.—Determine specific gravity at 15°C. as directed in Chap. XI, under analysis of fats and oils.

Viscosity.—Determine viscosity at 100°F. by the pipette method or by means of the Saybolt viscosimeter, as described in Chap. XI.

Unsaponifiable Matter, Unoxidized, and Oxidized Fatty Acids.—Determine exactly as directed under analysis of fats and oils in Chap. XI.

Iodine Value and Melting Point of Unoxidized Fatty Acids.—Determine as directed in Chap. XI.

Sulfur.—Weigh accurately about 3 g. into a platinum dish, and mix thoroughly with about 20 g. of pure, anhydrous sodium carbonate, using a stiff platinum wire. The consistency of the mixture should be such that any material sticking to the wire can easily be brushed off. Cover the mixture with a layer of sodium carbonate a few millimeters thick. Heat to dull redness in a muffle furnace until most of the carbon is consumed; the ignition should be continued at least 30 min. after flame combustion has ceased, or else the percentage of sulfur obtained will be too low. Cool. Transfer the residue to a beaker, and dissolve the mass in hot water. Filter, receiving the filtrate in a 500-cc. volumetric flask, wash the paper until the filtrate no longer is alkaline toward phenolphthalein, cool, and make up to the mark.

Pipette exactly 200 cc. of the solution into a 400-cc. beaker. Add bromine water until the color is not discharged on stirring, acidify with hydrochloric acid, and boil to expel the excess of bromine. Precipitate, filter, wash, and ignite and weigh the sulfur as barium sulfate by the procedure described in Chap. VIII under analysis of sodium chloride. Calculate and report percentage of sulfur.

$$= \frac{\text{g. BaSO}_4 \times 34.}{\text{g. sample weighed}}$$

Chlorine.—Pipette 200 cc. of the solution prepared for the determination of sulfur, as described above, and determine chlorine by either the Mohr method or the Vollhardt method, described in Chap. VIII. Calculate and report percentage of chlorine.

Naphtha: Loss at 100°C.—Weigh accurately about 5 g. into a weighed platinum dish. Place in an oven at 100 to 105°C. overnight. Cool in a desiccator, and weigh. Calculate percentage of loss, and report as percentage of naphtha. Use the residue for determining ash.

Distillation Method.—Measure 100 cc. of the oil in a graduated cylinder, and transfer to a 250-cc. side-arm, distilling flask. Close the flask with a cork carrying a thermometer, range 0 to 200°C. Connect the flask to a water-cooled condenser. Heat the contents of the flask with a small free flame. Note the temperature at which distillation begins. Collect the distillate in a graduated cylinder. Regulate the flame so that the distillate collects at a rate of about 1 cc. per minute. Continue the distillation until the oil begins to decompose, which is shown by the appearance of white fumes in the flask and an odor of sulfur dioxide in the distillate. Note the highest temperature attained, read the volume of the distillate, and calculate percentage of naphtha. Report "naphtha: distillate from ——— to

$$\text{Per cent naphtha} = \frac{\text{cc. distillate} \times \text{sp. gr. distillate}}{\text{cc. or gr. sample}}$$

Specific Gravity.—Determine the specific gravity of the distillate, obtained as described above, by the Westphal balance or other method as described in Chap. XI.

Ash.—Ignite the residue obtained in determining naphtha by loss at 100°C., first setting fire to the oil by playing a flame into the dish, and then igniting over a flame or in a muffle furnace until all carbon is consumed. Cool in a desiccator, and weigh. Calculate and report percentage of ash.

$$\text{Per cent} = \frac{\text{g. sample weighed for determination of naphtha}}{\text{g. sample weighed for determination of naphtha}}$$

NITROCELLULOSE FINISHES AND THEIR CONSTITUENTS

Nitrocellulose lacquers are used to supplement or replace the water finishes used on light leathers and, applied in much heavier coats, to impart an artificial grain to leather splits and in the manufacture of patent leather. Some leather manufacturers compound their own lacquers, purchasing the basic materials; others make use of lacquer finishes sold in a form requiring only thinning or the addition of pigment or dye before application to the leather.

Nitrocellulose, or cellulose nitrate, also known as pyroxalin, is made by nitrating purified cotton linters or other cheap, pure cellulose with a mixture of nitric and sulfuric acids. The product is not a definite chemical compound but consists of a mixture of nitrates. The properties of a nitrocellulose vary with the nitrogen content, which is determined by the strength of acid employed, temperature, and time of contact of acid with cellulose. Pyroxalins containing more than about 12.5 per cent nitrogen are too insoluble for use in lacquers; the nitrocellulose used in lacquers contains from 11.0 to 12.5 per cent nitrogen. After nitration, the cotton is carefully freed from acid and undesirable by-products by a series of washings. The water is then displaced by alcohol, since the presence of water in the product would cause the nitrocellulose to be precipitated from its solutions in organic solvents, while dry nitrocellulose is too explosive to be handled with safety. The product sold generally contains about 30 per cent alcohol.

For application as a lacquer, nitrocellulose is dissolved in a suitable mixture of organic solvents. A very large number of solvents have been suggested, and a great many are actually used. The esters and ketones are the best solvents, but many of the alcohols, while not solvents for nitrocellulose in themselves, may be admixed in rather large proportions with the true solvents without impairing the solvent properties of the latter. Hydrocarbons, particularly the aromatic ones, are sometimes added as diluents in order to reduce the cost. In any formula, proper

balance must be maintained between solvents and non-solvents and between low- and high-boiling solvents, in order to obtain the desired result.

As a pure nitrocellulose film is extremely brittle, the lacquer must contain a substance, known as a plasticizer, that will form a solid solution with the pyroxalin and render the film tough and elastic. Oils, especially castor oil, and camphor were the original materials used for this purpose but have been largely supplanted by high-boiling esters.

Resins are sometimes incorporated with the lacquer, being somewhat cheaper than nitrocellulose, and because they increase the gloss and adhesion of the coat.

For opaque coatings, pigments are mixed with the lacquer. The pigments employed are, in general, the same as those used for water finishes but are generally ground in the lacquer itself or in the plasticizer that is to be used. For clear coatings, spirit-soluble dyes are used.

NITROCELLULOSE

The most important and characteristic property of a nitrocellulose is its viscosity in a solution of constant nitrocellulose content in a specified solvent or mixture of solvents. By varying the method of manufacture, nitrocelluloses of widely varying viscosities have been produced, suitable for the various uses to which lacquers are put. Once a nitrocellulose of specified viscosity has been found satisfactory and adopted for use, care must be taken that no change is made in the viscosity type of cotton employed. Viscosity is generally determined by the "falling-ball method" and reported in seconds. Pyroxalin is therefore sold as "0.5-sec. cotton," "20-sec. cotton," etc. For very low-viscosity cottons the falling ball method is not altogether satisfactory. For such materials, the capillary tube viscosimeter or a viscosimeter of the torsion type, such as the MacMichael instrument, may be employed.

The methods given below are those of the Hercules Powder Company (5) (abridged). The falling ball method has very recently been adopted as a tentative standard, practically as given here, by the American Society for Testing Materials.

Viscosity (Falling Ball Method).—The apparatus consists of a glass cylinder, 355 mm. (14 in.) long, of a uniform diameter of 25.0 ± 0.5 mm., closed at the bottom with a cork wrapped in tin foil, and supported ver-

tically. The cylinder has two marks, 254 ± 0.8 mm. (10 in.) apart, 2 in. from either end. The ball is a $\frac{5}{16}$ -in. steel ball bearing, of diameter 0.793 to 0.797 mm., and weighing from 2.046 to 2.054 g. A large proportion of the $\frac{5}{16}$ -in. ball bearings on the market are said to comply with these specifications.

The specifications, particularly those governing the diameter of the tube, must be followed very closely. Even the 0.5-mm. tolerance creates a variation in result of 2.2 per cent.

As the viscosity of nitrocellulose solutions is affected enormously by changes in temperature, it is necessary to make all measurements at a specified temperature. The temperature prescribed is $25^{\circ}\text{C.} \pm 0.1^{\circ}\text{C.}$ If numerous determinations are to be run, it is well to have an electrically regulated thermostat operating at that temperature. For occasional determinations, the tube and contents may be brought to approximately the specific temperature, the actual temperature noted on a thermometer sensitive to 0.1°C. , and a correction factor applied as given below.

For cottons other than 0.5 or 0.25 sec., prepare 200 g. of a solution containing 12.2 per cent dry nitrocellulose, 22.0 per cent denatured ethyl alcohol (Formula 1), 17.5 per cent ethyl acetate, and 48.3 per cent toluol. The nitrocellulose may be dried in an oven, spread out in a thin layer on a paper tray, for 5 hr. at 60°C. if the cotton has been wet with denatured ethyl alcohol, or for 8 hr. at 80°C. if wet with butyl alcohol. The tentative standard of the American Society for Testing Materials specifies that the cotton shall be dried to constant weight at 50°C. In drying nitrocellulose, the inflammable nature of the dried material must be remembered.

The ethyl acetate must comply with the tentative specifications of the American Society for Testing Materials (see below). The denatured alcohol shall contain not less than 92.3 per cent by weight of ethyl alcohol, denatured according to the government formula. The toluol shall have a specific gravity of 0.864 to 0.874 at $15\frac{1}{5}^{\circ}\text{C.}$, a 2°C. boiling range including the boiling point of toluene (110.4°C.), and be non-corrosive.

In preparing the solution, the ingredients are weighed with an accuracy of ± 0.02 g. Weigh 24.4 g. of nitrocellulose into an 8-oz. bottle, add the 44.0 g. of denatured alcohol and 96.6 g. of toluol, and finally the 35 g. of ethyl acetate. Stopper with a cork wrapped in tin foil, and shake slowly in a mechanical shaker until solution is complete. Then let the solution stand at about 25°C. (preferably in a constant-temperature bath) for not less than 24 hr.

In making the measurement, fill the cylinder with the solution, and let stand until the temperature of the solution is $25^{\circ}\text{C.} \pm 0.1^{\circ}\text{C.}$ This will require at least 1 hr. if the temperature of the solution was very different from that specified. If no constant-temperature bath is available, bring the solution to about 25°C. and note the temperature to 0.1°C. Drop the ball on the surface of the liquid, and note the time required for it to fall from the upper to the lower mark, using a stop watch. Report the viscosity in seconds. The time in seconds multiplied by 3.77 gives the viscosity in poises. If the measurement is made at a temperature other than 25.0°C. , find the viscosity at 25°C. by applying the equation

$$\log V = \log V_1 + 0.0207 (T_1 - T),$$

where V and V_1 are the viscosities at $25^\circ (T)$ and the observed temperature (T_1), respectively

For 0.5- and 0.25-sec. cottons, in which the time of fall (in the solution described above) is too short to be measured with even approximate accuracy, proceed exactly as above, but use one of the following solutions:

For 0.5-sec. cotton: nitrocellulose, 20 per cent; denatured alcohol (formula 1), 20 per cent; ethyl acetate, 16 per cent; toluol, 44 per cent.

For 0.25-sec. cotton: nitrocellulose, 25 per cent; denatured alcohol, 18.7 per cent; ethyl acetate, 15.0 per cent; toluol, 41.3 per cent.

A reading of 3 to 4 sec. with the solution prescribed for 0.5-sec. cotton is equivalent to 0.5 sec. with the solutions used for cottons of higher viscosity.

The prescriptions regarding concentration and composition of the solutions must be followed exactly. The viscosity of a nitrocellulose solution is *not* a linear function of concentration and is affected enormously by changes in kind or proportions of solvents.

Capillary Tube Method.—This method is applicable to pigmented as well as to clear solutions and was developed as an addition to the falling ball method. The apparatus, shown in Fig. 84, consists of a long capillary tube attached to a reservoir. The capillary is surrounded by a jacket (not shown) through which water at $25^\circ\text{C}.$ can be circulated. The apparatus is mounted on a substantial wooden base, with the capillary exactly parallel to the surface of the board, and the latter is provided with a spirit level and leveling screws so that the capillary can be made exactly horizontal while a measurement is being made. When the reservoir is being filled, one end of the base is raised and supported by a suitable brace so that the capillary is inclined at an angle of 45° . The reservoir is then vertical.

To carry out a viscosity measurement, tilt the instrument so that the reservoir is vertical, and fill it to the etched mark. Wait until the liquid comes to its equilibrium position before finally adjusting the level. Then, holding a finger over the end of the capillary, bring the instrument to the horizontal position. When the finger is removed, the liquid flows into the capillary. For comparative work, two marks are etched on the tube, at any convenient distance apart, and the time required for the meniscus to travel from one mark to the other is taken with a stop watch. For more scientific work, the tube must be calibrated, using a liquid of known absolute viscosity. During the measurement, water at $25^\circ\text{C.} \pm 0.1^\circ\text{C.}$ should be passed through the jacket.

To clean the instrument, attach the end of the capillary, through a catch bottle, to a suction pump, apply gentle suction, draw the nitrocellulose liquid into the bottle, and then pour the solvent into the reservoir, drawing it through the tube, until the latter is clean. Continue the suction until the tube is dry.

To calibrate the instrument, castor oil has been found suitable. The absolute viscosity of the sample employed must, however, have been recently determined by means of an instrument that gives results in terms of absolute viscosity. A mark is made on the tube about 10 cm. from the point where the capillary is welded to the reservoir. The tube is then mounted in the water jacket, and the reservoir filled with castor oil. The tube is lowered to the horizontal position, the end of the capillary being closed with a finger;

then the finger is removed, and the stop watch is started when the meniscus passes the mark. The point is marked that is reached by the meniscus when the elapsed time in seconds equals the viscosity in centipoises. For instance, if the viscosity of the oil is 665 centipoises, the mark is placed at the point reached in 665 sec. It is advisable to use a movable mark, such as a section of small-diameter rubber tubing, until the exact position of the mark has been established by several measurements, when a permanent mark can be made with a file.

The viscosity of any standard nitrocellulose solution in centipoises can then be determined by finding the time in seconds required for the solution to fill the capillary tube between the two marks. Strictly speaking, this is true only if the specific gravity of the solution is the same as that of the castor oil used for the calibration, but this is so nearly the case with most nitrocellulose solutions that it is permissible to think of the results in terms of absolute units.

For very viscous lacquers, it may be advisable to locate other points such that the time of flow is one-half or one-third that found when the original mark is used. Such auxiliary marks must be located by trial and not by linear measurement.

Having calibrated one tube, others may be calibrated against it, using any liquid of convenient viscosity.

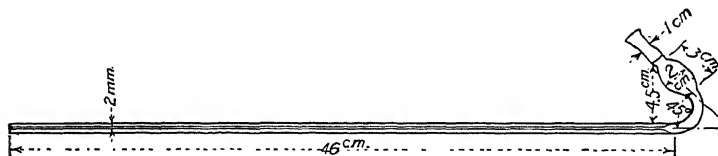


FIG. 84.—Capillary tube viscosimeter.

Other Tests.—Tentative specifications and tests for soluble nitrocellulose have very recently been issued by the American Society for Testing Materials (3). These specifications provide (a) that the nitrocellulose shall not be discolored and shall be free from lumps and foreign matter, such as charred particles; (b) that the ash content shall not exceed 0.3 per cent, calculated on the basis of dry-weight soluble nitrocellulose; (c) that the percentage of nitrogen (determined by means of the Dupont nitrometer) shall be within limits mutually agreed upon by buyer and seller; (d) that the stability shall be such that the methyl violet test paper shall not be completely changed to a salmon pink color in less than 20 min. (German stability test); (e) that the consistency (viscosity) shall be within the limits mutually agreed upon by buyer and seller for the particular type of nitrocellulose (determined by the falling ball method substantially

as described above); (*f, g, h*) that the solubility and appearance of the solution, film test, and toluol dilution test shall be equal to the "standard" for the particular type of soluble nitrocellulose. The solubility and appearance test is made by comparing the solution prepared for the viscosity measurement with a similar solution prepared from a nitrocellulose mutually agreed upon as standard. The film test is made by diluting the solution with an equal volume of normal butyl acetate and pouring the solution beside a similar solution made from standard nitrocellulose on a clean glass plate, which is allowed to dry in a nearly vertical position in a dust-free atmosphere. The sample is compared with the standard, paying particular attention to undissolved particles, poor flow, and poor gloss. The toluol dilution test is made with a solution of 12.2 g. of nitrocellulose (dried at 50°C. to constant weight) in 87.8 g. of normal butyl acetate. To 50 cc. of this solution, in a stoppered bottle, c.p. toluol is added from a burette, with shaking, and the first permanent separation of nitrocellulose is taken as the dilution value and expressed as percentage by volume of the solution taken (equals cubic centimeters of toluol added times 2). For a description of the determination of nitrogen by the Dupont nitrometer, and of the German stability test, consult the publications of the American Society for Testing Materials.

PLASTICIZERS

The methods employed depend entirely upon the type of plasticizer in question. The oil plasticizers, such as castor oil, should be tested by the methods given for fats and oils in Chap. XI. The high-boiling esters should be examined by methods given in "Allen's Commercial Organic Analysis" or similar encyclopedic works.

SOLVENTS AND DILUENTS

The list of solvents and diluents is very long and is constantly being added to as new substances are put on a commercial production basis. The American Society for Testing Materials has very recently issued tentative specifications for ethyl acetate, butyl acetate, and butanol (normal butyl alcohol). Similar specifications for the other important solvents and diluents will presumably be issued as rapidly as possible. These tentative specifications are given in Table 62.

TABLE 62.—TENTATIVE SPECIFICATIONS OF THE A. S. T. M. FOR ETHYL ACETATE, BUTYL ACETATE, AND BUTANOL (NORMAL BUTYL ALCOHOL)

	Ethyl acetate	Butyl acetate	Butanol (normal butyl alcohol)
Grade or purity, per cent.	85 to 88	85 to 88	98 to 100
Specific gravity at 20°C	0.883 to 0.888	0.870 to 0.875	0.810 to 0.815
Color.....	Water white	Water white	Water white
	{ Below 70°C.: none	{ Below 110°C.: none	{ 100 to 118°C.: 100 per cent
	{ Below 72°C.: not over 10 per cent	{ Below 120°C.: not over 15 per cent	{ Below 115°C.: not over 10 per cent
Distillation range.....	{ Above 80°C.: none	{ Below 125°C.: not less than 70 per cent	{ Below 105°C.: not over 2 per cent
		{ Above 145°C.: none	
Residue.....	None	None	None
Odor.....	Mild, non-residual	Mild, non-residual	Mild, non-residual
Water (miscible without cloud or turbidity in indicated proportions with 60° B _é . gasoline) .	1:10	All proportions	1:19
Acidity as acetic acid, per cent, not over.....	0.02	0.03	0.03
Ester value, per cent by weight.....	85 to 88	85 to 88	

Tentative methods for sampling and testing all lacquer solvents and diluents have been issued by the American Society for Testing Materials (3) and are reproduced below:

Sampling. *From Loaded Tank Car or Other Large Vessel.*—The composite sample taken shall be not less than 0.5 gal. and should consist of small samples of not more than 1 qt. each taken from near the top and bottom by means of a metal or glass container with removable stopper or top. This device, attached to a suitable pole, shall be lowered to the desired depth, when the stopper or top shall be removed and the container allowed to fill.

Barrels and Drums.—At least 5 per cent of all the packages in any shipment shall be represented in the sample. The purchaser may increase the percentage of packages to be sampled at his discretion, and it is recommended that every package be sampled in the case of expensive solvents that are bought in small quantity. A portion shall be withdrawn from about the

center of each package by means of a "thief" or other sampling device. The composite sample shall be not less than 1 qt. and shall consist of equal portions of at least 0.5 pt. from each package sampled.

Specific Gravity.—Determine at 20°C. by any method that is accurate to the third decimal place.

Color.—The sample and the standard mutually agreed upon by buyer and seller shall be compared in 50-cc. Nessler tubes against a white background. For a solvent to be rated water white, the visible color shall not be darker than that of a solution of 0.0030 g. of potassium dichromate in 1 l. of water.

Distillation.—The distillation test shall be conducted in accordance with the standard method of test for distillation of gasoline, naphtha, kerosene, and similar petroleum products (D 86) of the American Society for Testing Materials (given below), except that all observations of volumes of distillate shall be read at the temperatures specified for the individual solvent or diluent.

Residue.—Using a pipette, 5 cc. of the sample and of the standard shall be placed in separate porcelain evaporating dishes. These samples shall be allowed to evaporate in a hood for 24 hr. If any residue remains, its nature shall be noted, and the test for non-volatile solvents shall be made as follows:

Non-volatile Matter.—When the presence of non-volatile matter is indicated by the above test, place 100 cc. of the sample in a weighed porcelain dish and evaporate almost to dryness on the steam bath. Then heat in an oven at 100 to 110°C. to constant weight. Take the increase in weight of the dish as the non-volatile matter in the sample, and calculate as percentage, using the specific gravity of the sample determined as described above.

Residual Odor.—Determine for all solvents and diluents in which residual odor is an important property. Strips of heavy filter paper, of the same size and shape, shall be dipped to the same depth in beakers or wide-mouth bottles containing the sample and the standard. They shall then be attached to a piece of wood with thumb tacks, and at suitable intervals examined for difference in odor.

Water.—Transfer 5 cc. of the sample to a 100-cc. glass-stoppered cylinder, and add 60° B. gasoline in 5-cc. portions, shaking well after each addition. Water is indicated by turbidity. If turbidity develops, the standard shall be tested in the same way and compared.

Acidity.—Using a pipette, transfer 50 cc. of the sample to a small Erlenmeyer flask, and titrate with tenth-normal potassium hydroxide in 99 per cent methyl alcohol, using phenolphthalein as indicator. Determine the weight of the sample from its specific gravity, and report acidity as milligrams of potassium hydroxide per gram of sample.

Alkalinity.—When the results of the above test indicate that the sample is alkaline, transfer 50 cc. of the sample to a small Erlenmeyer flask, and titrate with tenth-normal sulfuric acid using methyl orange as indicator. Determine the weight of the sample from its specific gravity, and report alkalinity as milligrams of potassium hydroxide per gram of sample.

Ester Value (for Esters Only).—One to 2 grams of the sample shall be weighed in an ampoule, by first weighing the empty ampoule, warming

and filling, and then sealing off and reweighing. The ampoule shall be placed in a 200-cc. Erlenmeyer flask which contains 50 cc. of approximately half-normal alcoholic potassium hydroxide. The ampoule should be broken with a stirring rod, and the flask connected with a reflux condenser. The flask shall then be heated on a steam bath for 1 to 4 hr., depending upon the ester being tested. During the heating the set-up and contents should be shaken frequently, taking the usual precautions to lose none of the contents. After the apparatus has cooled, the condenser shall be washed down with distilled water and 3 drops of phenolphthalein added to the contents of the flask as an indicator. The contents of the flask shall be titrated with half-normal hydrochloric acid. Two blanks with alcoholic potassium hydroxide shall be run along with the sample. These blanks should check to the first decimal point. The result shall be reported as percentage of ester by weight, allowing in the calculations for acidity or alkalinity as determined above.

NOTE.—An optional method of weighing the sample is in a small weighing bottle, removing the stopper after introduction into the flask with a stirring rod, or by agitating the contents of the flask. Apparatus with glass joints should be used if available.

Copper Corrosion Test.—A copper corrosion test shall be run on solvents and diluents derived from coal tar and petroleum. A clean strip of mechanically polished pure sheet copper, about 1 in. square, shall be placed in a 4-in. porcelain evaporating dish and covered with 100 cc. of the sample. This shall be covered with a watch glass and heated on a steam bath for 30 min. The liquid shall be poured off and the copper examined for blackening. A slight tarnish shall be disregarded, but any marked blackening shall be cause for rejection.

STANDARD METHOD OF TEST FOR DISTILLATION OF GASOLINE, NAPHTHA, ETC. (A. S. T. M. D 86-27)

Apparatus

1. Flask.—The standard 100-cc. Engler flask is shown in Fig. 85, the dimensions and allowable tolerance being as follows:

	Centi- meters	Inches	Tolerances	
			Centi- meters	Inches
Diameter of bulb, outside.....	6.5	2.56	±0.2	±0.08
Diameter of neck, inside.....	1.6	0.63	±0.1	±0.40
Length of neck.....	15.0	5.91	±0.4	±0.16
Length of vapor tube.....	10.0	3.94	±0.3	±0.12
Diameter of vapor tube, outside....	0.6	0.24	±0.05	±0.02
Diameter of vapor tube, inside.....	0.4	0.16	±0.05	±0.02
Thickness of vapor tube wall.....	0.1	0.04	±0.05	±0.02

The position of the vapor tube shall be 9 cm. (3.55 in.) \pm 3 mm. above the surface of the liquid when the flask contains its charge of 100 cc. The tube is approximately in the middle of the neck and set at an angle of 75 deg. (tolerance \pm 3 deg.) with the vertical.

2. Condenser.—The condenser (Fig. S6) consists of a $\frac{9}{16}$ -in. (14.29 mm.) OD No. 20 Stubbs gage seamless brass tube, 22 in. (55.88 cm.) long. It is set at an angle of 75 deg. from the perpendicular and is surrounded with a cooling bath 15 in. long (38.1 cm.), approximately 4 in. (10.16 cm.) wide by 6 in. (15.24 cm.) high. The lower end of the condenser tube is cut off

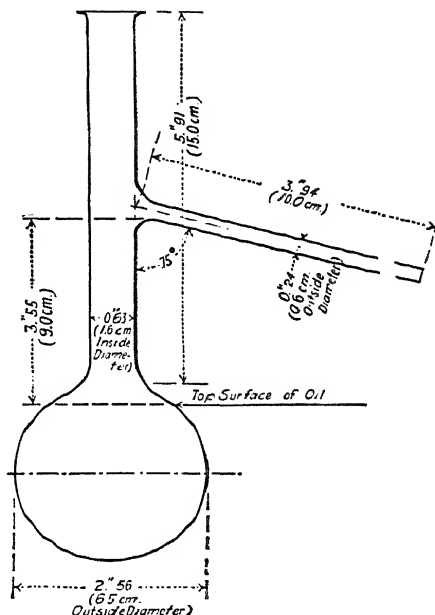


FIG. S5.—Standard Engler distillation flask.

at an acute angle and curved downward for a length of 3 in. (7.62 cm.) and slightly backward so as to ensure contact with the wall of the graduate at a point 1 to $1\frac{1}{4}$ in. (2.54 to 3.18 cm.) below the top of the graduate when it is in position to receive the distillate.

3. Shield.—The shield (Fig. S6) is made of approximately 22-gage sheet metal and is 19 in. (48.26 cm.) high, 11 in. (27.94 cm.) long, and 8 in. (20.32 cm.) wide, with a door on one narrow side, with two openings, 1 in. (2.54 cm.) in diameter, equally spaced, in each of the two narrow sides, and with a slot cut in one side for the vapor tube. The centers of these four openings are $8\frac{1}{2}$ in. (21.59 cm.) below the top of the shield. There are also three

b. Electric Heater.—The electric heater, which may be used in place of the gas flame, shall be capable of bringing over the first drop within the time specified below when started cold and of continuing the distillation at the uniform rate. The electric heater shall be fitted with an asbestos board top $\frac{1}{8}$ to $\frac{1}{4}$ in. (3.18 to 6.35 mm.) thick, having a hole $1\frac{1}{4}$ in. (3.18 cm.) in diameter in the center. When an electric heater is employed, the portion of the shield above the asbestos board shall be the same as with the gas burner, but the part below the board may be omitted.

6. Thermometers.—*a.* The A. S. T. M. low-distillation thermometer¹ shall conform to the following requirements. These specifications cover a total-immersion thermometer graduated in either centigrade or Fahrenheit degrees, as specified, the ranges being 0 to 300°C. or 30 to 580°F., respectively [0 to 400°C. or 30 to 760°F., respectively].

Type.—Etched stem, glass.

Liquid.—Mercury.

Range and Subdivision.—0 to 300°C. [400°C.] in 1°C. or 30 to 580°F. [760°F.] in 2°F.

Total Length.—378 to 384 mm. (14.88 to 15.12 in.).

Stem.—Plain front, enamel back, suitable thermometer tubing. Diameter, 6.0 to 7.0 mm. (0.24 to 0.28 in.).

Bulb.—Corning normal or equally suitable thermometric glass. Length, 10 to 15 mm. (0.39 to 0.59 in.). Diameter, 5.0 to 6.0 mm. (0.20 to 0.24 in.).

Distance to 0°C. or 32°F. Line from Bottom of Bulb.—100 to 110 mm. (3.94 to 4.33 in.) [25 to 35 mm. (0.98 to 1.38 in.).]

Distance to 300°C. [400°C.] or 572°F. [752°F.] Line from Top of Thermometer: 30 to 45 mm. (1.18 to 1.77 in.).

Filling above Mercury.—Nitrogen gas.

Top Finish.—Glass ring.

Graduation.—All lines, figures, and letters clear cut and distinct. The first and each succeeding 5°C. or 10°F. line to be longer than the remaining lines. Graduations to be numbered at each multiple of 10°C. or 20°F.

Immersion.—Total.

Special Marking.—“A. S. T. M. low- [high-] distillation,” a serial number and the manufacturer's name or trade-mark shall be etched on the stem.

Scale Error.—The error at any point of the scale when the thermometer is standardized as provided below shall not exceed 0.5°C. or 1°F.

Standardization.—The thermometer shall be standardized immersed in the testing bath to the top of the mercury column, at the ice point and at temperature intervals of approximately 50°C. or 100°F. up to 300°C. [370°C.] or 572°F. [700°F.].

Test for Permanency of Range.—After being subjected to a temperature of 280 to 290°C. [360 to 370°C.] or 540 to 560°F. [680 to 700°F.] for 24 hr., the accuracy shall be within the limit specified.

Case.—The thermometer shall be supplied in a suitable case on which shall appear the marking: “A. S. T. M. low [high] distillation, 0 to 300°C.

¹ Corresponding figures for the A. S. T. M. high-distillation thermometer are given in brackets.

[400°C.]” or “A. S. T. M. low [high] distillation, 30 to 580°F. [760°F.],” according to the type of thermometer.

NOTE.—For the purpose of interpreting these specifications, the following definitions apply:

The total length is the overall length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

7. **Graduate.**—The graduate shall be of the cylindrical type of uniform diameter, with a pressed or molded base and a lipped top. The cylinder shall be graduated to contain 100 cc., and the graduated portion shall be not less than 7 in. (17.18 cm.) nor more than 8 in. (20.32 cm.) long. It shall be graduated in single cubic centimeters, and each fifth mark shall be distinguished by a longer line. It shall be numbered from the bottom up at intervals of 10 cc. The overall height of the graduate shall be not less than $9\frac{3}{4}$ in. (24.8 cm.) nor more than $10\frac{1}{4}$ in. (26.0 cm.). The graduations shall not be in error by more than 1 cc. at any point on the scale.

Procedure

8. *a.* The condenser bath shall be filled with cracked ice,¹ and enough water added to cover the condenser tube. The temperature shall be maintained between 32 and 40°F. (0 and 4.45°C.).

b. The condenser tube shall be swabbed to remove any liquid remaining from the previous test. A piece of soft cloth attached to a cord or copper wire may be used for this purpose.

c. 100 cc. of the product shall be measured in the 100-cc. graduated cylinder at 55 to 65°F. (12.8 to 18.3°C.) and transferred directly to the Engler flask. None of the liquid shall be permitted to flow into the vapor tube.

d. The thermometer² provided with a cork shall be fitted tightly into the flask so that it will be in the middle of the neck and so that the lower end of the capillary tube is on a level with the inside of the bottom of the vapor outlet tube at its junction with the neck of the flask. The thermometer shall be approximately at room temperature when placed in the flask.

e. The charged flask shall be placed in the $1\frac{1}{4}$ -in. (3.18 cm.) opening in the 6 by 6-in. (15.24 by 15.24 cm.) asbestos board with the vapor outlet tube inserted into the condenser tube. A tight connection may be made by means of a cork through which the vapor tube passes. The position of the flask shall be so adjusted that the vapor tube extends into the condenser tube not less than 1 in. (2.54 cm.) nor more than 2 in. (5.08 cm.).

f. The graduated cylinder used in measuring the charge shall be placed, without drying, at the outlet of the condenser tube in such a position that the condenser tube shall extend into the graduate at least 1 in. (2.54 cm.)

¹ Any other convenient cooling medium may be used.

² For products having an initial boiling point of 212°F. (100°C.) or higher, the high-distillation thermometer shall be used; for all other products, the low-distillation thermometer shall be used.

but not below the 100-cc. mark. Unless the temperature is between 55 and 65°F. (12.8 and 18.3°C.) the receiving graduate shall be immersed up to the 100-cc. mark in a transparent bath maintained between these temperatures. The top of the graduate shall be covered closely during the distillation with a piece of blotting paper or its equivalent, cut so as to fit the condenser tube tightly.

9. When everything is in readiness, heat shall be applied at a uniform rate, so regulated that the first drop of condensate falls from the condenser in not less than 5 nor more than 10 min. The distillation thermometer shall be read 2 min. after heat is applied, and the indication recorded as the "correction temperature." This figure is of significance only in cases when there is a question as to the accuracy¹ of the initial boiling point, as subsequently determined. When the first drop falls from the end of the condenser, the reading of the distillation thermometer shall be recorded as the *initial boiling point*. The receiving cylinder shall then be moved so that the end of the condenser tube shall touch the side of the cylinder. The heat shall then be so regulated that the distillation proceeds at a uniform rate of not less than 4 nor more than 5 cc. per minute. The volume of distillate collected in the cylinder shall be observed and recorded, to the nearest 0.5 cc., when the mercury of the thermometer reaches each point that is an even multiple of 25°C. or the Fahrenheit equivalent of this point 50, 75, 100, 125°C., etc., or 122, 167, 212, 257°F., etc.). If preferred, the

¹ The initial boiling point is one of the observations which it is customary to report as indicative of the quality of gasoline. It is a point which is very difficult to check, especially when duplicate tests are made at different room temperatures, and it has not been found practical to devise an accurate method of correcting for this unavoidable variation in operating conditions. The practical significance of initial boiling point is not regarded as sufficient to warrant requiring that tests be conducted under regulated conditions of room temperature. The following directions are included as an expedient intended to obviate some of the difficulties that develop on account of the practice of including initial boiling-point limits in specifications for the purchase and sale of gasoline:

If the correction temperature is below 70°F. (21°C.) or above 80°F. (27°C.), the observed initial boiling point, if it is below 150°F. (66°C.), may be considered incorrect by an amount not less than one-third the difference between the correction temperature and 75°F. (24°C.). In case there is a dispute between buyer and seller, the observed initial boiling point figures obtained by all parties shall be revised according to the following formula:

Revised initial boiling point =

$$\left\{ \begin{array}{l} \text{observed initial} \\ \text{boiling point} \end{array} \right. + \frac{\text{correction temperature (°F)} - 75}{3}$$

If all of the revised figures fall within the specification limit, the gasoline in question shall be considered as passing; otherwise arrangements shall if, possible, be made to conduct a distillation test with the room temperature maintained between the limits of 70 and 80°F. (21 and 27°C.) inclusive.

reading of the distillation thermometer may be observed and recorded when the level of the distillate reaches each 10-cc. mark on the graduate. In case a product is being tested to ascertain whether or not it conforms with a given specification, all necessary observations shall be made and recorded, whether or not they are included in the series ordinarily employed by the laboratory making the test.

When the liquid residue in the distillation flask is approximately 5 cc., the heat may be increased because of the presence of heavy ends which have relatively high boiling points. However, no further increase of heat shall be applied after this adjustment. The 4- to 5-cc. rate can rarely be maintained from this point to the end of the distillation, but in no case shall the period between the point when approximately 5 cc. of liquid remains in the flask and the end point be more than 5 min.

The heating shall be continued until the mercury reaches a maximum and starts to fall consistently. The highest temperature observed on the distillation thermometer shall be recorded as the *maximum temperature* or end point. Usually this point will be reached after the bottom of the flask has become dry.

The total volume of the distillate collected in the receiving graduate shall be recorded as the *recovery*.

The cooled residue shall be poured from the flask into a small cylinder graduated in 0.1 cc., measured when cool, and the volume recorded as

The difference between 100 cc. and the sum of the recovery and the residue shall be calculated and recorded as *distillation loss*.

10. Accuracy.—With proper care and attention to detail, duplicate results obtained for initial boiling point and maximum temperature, respectively, should not differ from each other by more than 6°F. (3.3°C.). Duplicate readings of the volume of distillate collected in the cylinder when each of prescribed temperature points is reached should not differ from each other by more than 2 cc. In case observations are made on the basis of prescribed percentage points, the differences in temperature readings should not exceed the amounts equivalent to 2 cc. of distillate at each point in question.

11. Correction for Barometric Pressure.—The actual barometric pressure shall be ascertained and recorded, but no correction shall be made except in case of dispute. In such cases the temperature points shall be corrected to 760 mm. (29.92 in.), by the use of the Sydney Young equation, as follows

For centigrade readings:

$$C_c = 0.00012(760 - P)(273 + t_c)$$

For Fahrenheit readings:

$$C_f = 0.00012(760 - P)(460 + t_f)$$

in which C_c and C_f are, respectively, corrections to be added to the observed temperature t_c or t_f , and P is the actual barometric pressure in millimeters of mercury.

The following table is a convenient approximation of the corrections as calculated by the above equation.

Temperature range		Correction ¹ per 10 mm. difference in pressure	
Degrees centigrade	Degrees fahrenheit	Degrees centigrade	Degrees fahrenheit
10 to 30	50 to 86	0.35	0.63
30 to 50	86 to 122	0.38	0.68
50 to 70	122 to 158	0.40	0.72
70 to 90	158 to 194	0.42	0.76
90 to 110	194 to 230	0.45	0.81
110 to 130	230 to 266	0.47	0.85
130 to 150	266 to 302	0.50	0.89
150 to 170	302 to 338	0.52	0.94
170 to 190	338 to 374	0.54	0.98
190 to 210	374 to 410	0.57	1.02
210 to 230	410 to 446	0.59	1.06
230 to 250	446 to 482	0.62	1.11
250 to 270	482 to 518	0.64	1.15
270 to 290	518 to 554	0.66	1.19
290 to 310	554 to 590	0.69	1.24
310 to 330	590 to 626	0.71	1.28
330 to 350	626 to 662	0.74	1.32
350 to 370	662 to 698	0.76	1.37
370 to 390	698 to 734	0.78	1.41
390 to 410	734 to 770	0.81	1.45

¹ To be added in case barometric pressure is below 760 mm.; to be subtracted in case barometric pressure is above 760 mm.

MIXED LACQUERS

The complete quantitative analysis of a lacquer is an almost impossible task, because of the infinite number of possible combinations of solvents, diluents, and plasticizers that may be employed. It is, however, possible to determine some constituents of a lacquer with fair accuracy and to obtain valuable qualitative information regarding the others. S. P. Wilson (12) gives the following outline of a procedure:

Total Solids.—Weigh accurately from 5 to 10 g. of the lacquer in a tared dish, add 100 cc. of a 2:1 ether-alcohol mixture, stir till the solution is homogenous, and bring it to a boil on a steam bath. Add 25 cc. of water, with constant stirring. The pyroxalin is precipitated in stringy masses. Evaporate the solution to dryness on the steam bath, dry for 2 hr. at 100°C., cool in a desiccator for $\frac{1}{2}$ hr., and weigh.

If the lacquer sample is evaporated directly, it is difficult to expel the last of the vapors, because of the impervious skin that forms.

Oils and Resins.—Extract a portion of the residue, weighed accurately, in a Soxhlet extractor, first with chloroform and then with absolute alcohol, evaporate the combined extracts in a tared dish, and weigh. Examine the residue by the methods given for the analysis of oils and resins in the larger texts dealing with these substances.

Solvents.—Place 100 to 200 g. of lacquer in a round-bottomed Pyrex flask, and distill by passing a current of steam through the liquid or by adding 200 cc. of water and distilling from an oil bath. The distillate generally forms two layers, a homogeneous distillate indicating that the solvent is of the absolute alcohol-ethyl acetate type, which is miscible with water. Saturate the water layer with salt, which forces much of the water-soluble alcohol and ester into the oily layer. Separate the layers with a separatory funnel. Dry the oily layer by adding anhydrous calcium chloride. Distill the oily layer, using a fractionating column, and collect fractions at suitable temperature intervals. For each fraction, determine saponification value and percentage insoluble in cold 95-per cent sulfuric acid (hydrocarbons). From the boiling range, saponification values, and acid-insoluble percentages, the composition of the solvent can be determined approximately. By fractionating the water layer, the alcohols can be partially separated and identified.

Pigment.—By precipitating the pyroxylin with chloroform or water, the nitrocellulose and pigment are brought down together in slimy masses. The solvent is decanted off, the pyroxalin redissolved in a very large excess of acetone, and the pigment separated by centrifuging. The nitrocellulose solution is decanted off, the pigment washed with acetone, collected, and weighed. Qualitative and quantitative analysis of the pigment can then be performed by the usual methods.

Viscosity.—Determine the viscosity of the lacquer by the methods given under analysis of nitrocellulose. The results, of course, are purely comparative.

Acidity.—Perform the copper corrosion test described under solvents and diluents.

References

1. ALLEN, A. H.: *Commercial Organic Analysis*, 5th ed., P. Blakiston's Son & Co., New York, 1923-1929.
2. AMERICAN LEATHER CHEMISTS ASSOCIATION: *Methods*, *J. Am. Leather Chem. Assoc.*, **22**, 567, 1927.
3. AMERICAN SOCIETY FOR TESTING MATERIALS: A. S. T. M. Tentative Standards (issued annually), 1929; A. S. T. M. Standards (issued triennially), vol. 2, 1927.
4. GNAMM, H.: "Die Fettstoffe in der Lederindustrie," Wiss. Verlagsges. m. b. h., Stuttgart, 1926.
5. HERCULES POWDER CO.: "Nitrocellulose Handbook," Wilmington, Del., 1930.
6. LONG, J. S., and J. G. SMULL: *Control Methods for Boiling Drying Oils*, *Ind. Eng. Chem.*, **17**, 138, 1925.
7. PROCTER, H. R.: "Leather Industries Laboratory Book," 2d ed., E. & F. N. Spon, London and New York, 1908.

8. SCOTT, W. W., ed.: "Standard Methods of Chemical Analysis," 4th ed., revised, D. Van Nostrand Company, Inc., New York, 1927.
9. SUTERMEISTER, EDWIN: "Casein and Its Industrial Applications," A. C. S. Mon. Ser., The Chemical Catalog Company, Inc., New York, 1927.
10. THORNTON, W. M., JR.: "Titanium," A. C. S. Mon. Ser., The Chemical Catalog Company, Inc., New York, 1927.
11. WILSON, JOHN ARTHUR: "The Chemistry of Leather Manufacture," 2d ed., vol II, A. C. S. Mon. Ser., The Chemical Catalog Company, Inc., New York, 1929.
12. WILSON, S. P.: "Pyroxalin Enamels and Lacquers," 2d. ed., D. Van Nostrand Company, Inc., New York, 1927.

CHAPTER XIII

PREPARATION OF STANDARD SOLUTIONS

A standard solution is one that contains a known weight of a reagent in a known volume of solution. By determining the volume of standard solution required to complete a given reaction, the weight of reagent consumed may be calculated, from which the weight of the substance acted upon by the reagent may be computed. A standard solution may be of any strength whatsoever as long as its strength is known with accuracy. It is generally most convenient to have standard solutions contain a simple decimal fraction of a gram-equivalent of the reagent in 1 l. A standard solution containing exactly 1 gram equivalent in 1 l. of solution is a *normal* solution, abbreviated to "*N*" or "*1-N*." Depending upon particular conditions, half-normal (*0.5-N*), fifth-normal (*0.2-N*), tenth-normal (*0.1-N*), and fiftieth-normal (*0.02-N*) solutions may be required. Very often, when a standard solution is to be used for analyzing one material only, it is convenient to have it of such strength that the concentration of the material analyzed, in percentage or in pounds per gallon or any other desired units, can be read off directly from the burette or obtained from the burette reading with the minimum of calculation. The preparation of such special solutions has been described in the text in connection with the analysis of pickle liquors and some other materials.

When a reagent can be obtained in a very pure state, when that reagent is completely unchanged on storage, and when the reagent is of such a nature that portions thereof can be weighed off with great accuracy and without errors due to giving up or taking on moisture, it is possible to prepare a standard solution by weighing off the required number of grams of reagent and dissolving it in the required volume of solution. Examples of materials from which standard solutions can be prepared in this way are potassium chloride, potassium dichromate, sodium oxalate, and sodium carbonate. In the majority of cases, however, it is not possible to prepare a standard solution by direct weighing of the

reagent, for the reason that most of the reagents commonly employed in volumetric analysis contain either a variable amount of water or other impurities or else give solutions that change in strength somewhat upon standing. Most of the acids, alkalies, oxidizing agents, and reducing agents commonly employed in standard solutions fall in one or the other (or both) of these categories. In such cases, the standard solution must first be prepared so as to contain roughly the required quantity of reagent in a given volume; then its exact strength must be determined, either by comparison with a solution whose exact strength has previously been determined or by gravimetric analysis; and finally the strength may be adjusted to the desired value by dilution or fortification, followed by a recheck of the normality. It is not necessary to adjust a standard solution to exactly its nominal normality, so long as the actual exact normality is known. When the final adjustment is dispensed with, a factor is calculated by which the observed volumes of the solution as it stands must be multiplied to obtain the corresponding volumes of a solution having exactly the nominal normality. This factor is simply the actual normality divided by the nominal. For example, if a solution nominally $0.1-N$ is actually $0.0954-N$, every volume of solution consumed must be multiplied by $0.0954/0.1000$, or 0.954 , in order to obtain the corresponding volume of exactly $0.1-N$ solution.

Whether solutions are adjusted to exact nominal normalities or left as they may happen to be upon preparation and a factor employed is largely a matter of personal preference. The authors always adjust tenth-normal acids and alkalies, which are used for the analysis of many materials and by many individual analysts, to the nominal normality. They do not so adjust solutions of oxidizing and reducing agents, such as tenth-normal sodium thiosulfate, iodine, potassium permanganate, etc.

ACIDS AND ALKALIES

The authors use as a primary standard in acidimetry a tenth-normal solution of sulfuric acid, standardized gravimetrically and used only for standardization purposes. This system was adopted because it permits tenth-normal sodium hydroxide to be compared directly with this standard sulfuric acid, using methyl red indicator. The most important acidimetric determination carried out in a leather laboratory is the titration of

excess sulfuric acid by tenth-normal sodium hydroxide in the determination of ammonia in the Kjeldahl method for nitrogen in leather. In this determination, methyl red is employed, and it is desirable that the standardization of tenth-normal sodium hydroxide should be carried out under the same conditions as those prevailing in the nitrogen determination.

Preparation of Standard Tenth-normal Sulfuric Acid.—Prepare approximately tenth-normal sulfuric acid by dissolving 6 cc. of the purest sulfuric acid (sp. gr. 1.84) in 2 l. of solution. Pipette three 25-cc. portions of this solution into 400-cc. beakers, dilute to about 200 cc., add a few cubic centimeters of concentrated hydrochloric acid, and heat to boiling. To the hot solution add 10 cc. of a 10-per cent solution of barium chloride, adding the reagent drop by drop from a pipette, with constant stirring. Allow precipitate to settle overnight. Filter through Whatman's No. 44 filter paper or its equivalent, and wash until the precipitate is free from chlorides. Dry the paper and precipitate at about 100°C., and ignite in a weighed porcelain crucible. Apply gentle heat at the start, so that the paper chars without bursting into flames. When charring is complete, apply the full heat of an ordinary Bunsen burner (not a blast lamp or Meker burner), and ignite till all carbon is consumed. Incline the crucible during the ignition so as to allow free access of air to the interior. Cool the crucible and contents in a desiccator, and weigh. Reignite for 10 min., cool, and reweigh. Repeat till a constant weight is obtained. Using the average of 2 or more results agreeing within 0.0005 g., calculate the volume of approximately tenth-normal solution that contains 9.8080 g. of sulfuric acid.

$$\begin{aligned} \text{G. H}_2\text{SO}_4 \text{ per cc.} &= \frac{\text{g. BaSO}_4 \times}{25} \\ \text{Cc. required} &= \frac{9.8080}{\text{g. H}_2\text{SO}_4 \text{ per cc.}} \end{aligned}$$

Carefully measure the required volume of approximately tenth-normal sulfuric acid into an accurately calibrated 2-l. flask, using accurately calibrated pipettes or flasks calibrated "to deliver." As it is much easier to adjust the normality of a solution that is a little too strong than that of one which is too weak, add 2 cc. more than the calculated volume. Dilute to the mark with distilled water, at the temperature used in calibrating the flask. Mix thoroughly. Pour off enough of the solution to fill a 100-cc. volumetric flask exactly to the mark, being careful not to waste any of the solution. From this 100-cc. portion, pipette three 25-cc. aliquots, and determine sulfuric acid by precipitation as barium sulfate, exactly as described above. Calculate the normality of the solution.

$$\text{Normality} = \frac{\text{g. BaSO}_4 \times 0.4202}{0.04904 \times 25}$$

If the normality found lies in the range 0.1002 to 0.0998 inclusive, the solution may be regarded as exactly tenth-normal and used as such without further adjustment, since such a discrepancy amounts to only 0.1 cc. in a

50-cc. titration. If the normality exceeds 0.1002, add 1.9 cc. water for each ten-thousandth by which the normality exceeds 0.1000 to the 1,900 cc. of solution left after withdrawing 100 cc. for use in standardizing.

Preserve the solution in a well-stoppered bottle, and use it only for standardizing tenth-normal sodium hydroxide as described below.

Preparation of Stock Ten-normal Sodium Hydroxide Solution.—Dissolve approximately 900 g. of stick sodium hydroxide in approximately 2 l. of water. Cool to room temperature, transfer to a rubber-stoppered bottle, and let stand until the carbonate has settled out. Siphon off the clear solution into a second bottle equipped with a 2-hole rubber stopper carrying a large soda-lime tube and a delivery tube extending nearly to the bottom of the bottle. The outer end of the delivery tube is closed with a rubber tube and pinchcock. Determine the approximate normality of the solution as follows: Pipette 10 cc. into a 1-l. volumetric flask, and dilute to the mark with recently boiled distilled water. Titrate aliquots of this solution with tenth-normal sulfuric acid, using methyl red indicator.

$$\text{Normality stock solution} = \frac{\text{cc. } 0.1\text{-}N \text{ H}_2\text{SO}_4 \times 10}{\text{cc. NaOH solution titrated}}$$

Do not adjust the normality of the stock solution, but use the normality in calculating the volume to be taken to prepare normal and tenth-normal sodium hydroxide.

Preparation of Normal Sodium Hydroxide.—Measure into a 2-l. volumetric flask the volume of sodium hydroxide stock solution required to give 2 l. of normal sodium hydroxide, and dilute to the mark with recently boiled distilled water. Pipette 50 cc. of the solution into a 500-cc. volumetric flask, dilute to the mark with recently boiled distilled water, and standardize by titrating aliquots of this solution with tenth-normal sulfuric acid, using methyl red indicator. Calculate the normality of the approximately normal sodium hydroxide.

$$\text{Normality} = \frac{\text{cc. } 0.1\text{-}N \text{ H}_2\text{SO}_4}{\text{cc. NaOH solution titrated}}$$

Do not adjust the normality of the approximately normal sodium hydroxide, but record the normality found, and employ the proper factor in using the solution.

Preparation of Tenth-normal Sodium Hydroxide.—Measure accurately from a burette into a 2-l. volumetric flask the volume of approximately normal (or ten-normal) sodium hydroxide required to produce 2 l. of tenth-normal sodium hydroxide, and dilute to the mark with recently boiled distilled water. Pour 100 cc. of the solution into a 100-cc. volumetric flask for use in standardizing, taking care not to waste any of the remaining 1,900 cc. Fill a burette with the tenth-normal sodium hydroxide. Measure three 25-cc. portions of tenth-normal sulfuric acid, prepared for use in standardizing only, into Erlenmeyer flasks, and dilute to about 100 cc. with recently boiled distilled water. Add 3 drops of methyl red indicator, and titrate with the tenth-normal sodium hydroxide solution until the red color is discharged. A single drop of tenth-normal sodium hydroxide should

change the solution from a clear pink to a clear yellow. Calculate the normality of the sodium hydroxide solution. If the normality found lies

$$\text{Normality} = \frac{25}{\text{cc. NaOH solution} \times 10}$$

in the range 0.1002 – 0.0998, do not adjust further, and consider the reagent as 0.1000-*N*, since a difference of this magnitude corresponds to a difference in burette reading of not more than 0.05 cc. for a 25-cc. titration. If the normality found is more than 0.1002, add 1.9 cc. water to the 1,900 cc. of tenth-normal solution for every ten-thousandth by which the normality found exceeds 0.1000, or add 0.19 cc. of tenth-normal sodium hydroxide for every ten-thousandth by which the normality found is less than 0.1000, and restandardize against the tenth-normal sulfuric acid used for standardizing only.

The greatest care should be taken in this standardization, as the tenth-normal sodium hydroxide is used in turn to standardize the standard acid solutions used in actual work. The normality of tenth-normal sodium hydroxide should be checked frequently.

Standardization of Tenth-normal Sodium Hydroxide Using Phenolphthalein. Due to the almost inevitable presence of carbonate in sodium hydroxide solutions, the apparent strength of a tenth-normal sodium hydroxide solution will be different when the solution is used to titrate weak acids, using phenolphthalein indicator, from what it is when the solution is used to titrate strong acids, using methyl red indicator. When phenolphthalein is to be used, standardize the tenth-normal sodium hydroxide against 25-cc. aliquots of standard sulfuric acid, using this indicator and taking as the end point the formation of a very faint pink color. Calculate the normality of the sodium hydroxide and its factor. Record on the bottle: "Factor for use with phenolphthalein = ———."

$$\text{Normality} = \frac{25}{\text{cc. NaOH} \times 10}$$

$$\text{Factor} = \frac{\text{Normality found}}{0.1} = \text{normality} \times 10$$

When using tenth-normal sodium hydroxide with phenolphthalein indicator, the volume consumed in titration must be multiplied by this factor to get the corresponding volume of exactly tenth-normal sodium hydroxide.

Preparation of Normal and Tenth-normal Sulfuric and Hydrochloric Acids.—Prepare 2 l. of approximately normal hydrochloric acid and sulfuric acid by dissolving 70 cc. of sulfuric acid (sp. gr. 1.84) and 175 cc. of hydrochloric acid (sp. gr. 1.20), respectively, in 2 l. Determine the normality of each solution by titrating aliquots of a 1:10 dilution with tenth-normal sodium hydroxide. The normality found should be more than 1.0. Calculate the volume which, when diluted, will make exactly 2 l. of exactly normal acid.

$$\text{Vol. required} = 2,000/\text{normality found}$$

Measure this volume into a 2-l. volumetric flask, and dilute to the mark. Standardize again by titrating aliquots of a 1:10 dilution of each solution

with tenth-normal sodium hydroxide, and adjust again if necessary until the normality lies in the range 1.002 to 0.998.

Having prepared normal sulfuric acid and hydrochloric acid, prepare tenth-normal solutions by diluting 200 cc. of each normal solution to 2 l. and standardizing against tenth-normal sodium hydroxide. If the first solution prepared is not exactly tenth-normal, adjust by adding water or normal acid as described under the preparation of tenth-normal sodium hydroxide.

Preparation of Fiftieth-normal Acids and Alkalies.—Measure accurately 200 cc. of the tenth-normal solution into a 1-l. volumetric flask, and dilute to the mark with recently boiled distilled water. No standardization is necessary, provided the accuracy of the tenth-normal solution can be guaranteed.

SILVER NITRATE

Preparation of Standard Potassium Chloride Solution.—Dry about 10 g. of pure, recrystallized potassium chloride in the oven at 110°C. overnight. Place the dried salt in a glass-stoppered weighing bottle, and keep it in a desiccator over sulfuric acid. Weigh accurately 7.4560 g. of potassium chloride into a 1-l. volumetric flask, and dissolve and dilute to the mark with water. The resulting solution is exactly tenth-normal.

Preparation of Tenth-normal Silver Nitrate.—Weigh off from 17.5 to 18.0 g. of pure silver nitrate, dissolve in water, and dilute to 1 l. The resulting solution should be somewhat stronger than tenth-normal. Measure accurately three 25-cc. aliquots of the tenth-normal potassium chloride solution, dilute to about 150 cc., add a few drops of potassium chromate indicator, and titrate with the tenth-normal silver nitrate solution. The end point is the formation of a permanent brick-red precipitate of silver chromate. Calculate the normality of the silver nitrate solution.

$$\text{Normality} = \frac{25}{\text{cc. approx. } 0.1-N \text{ AgNO}_3 \times 10}$$

Calculate the volume of silver nitrate solution which, when diluted to 1 l., will produce 1 l. of exactly tenth-normal silver nitrate.

$$\text{Vol. required} = \frac{100}{\text{normality of AgNO}_3}$$

Measure accurately this volume into a 1-l. volumetric flask, dilute to the mark, and restandardize against tenth-normal potassium chloride as described above.

POTASSIUM PERMANGANATE

Preparation of Tenth-normal Potassium Permanganate.—Weigh roughly 6.5 g. of potassium permanganate, dissolve in about 500 cc. of hot water, filter the solution through asbestos, if necessary, to remove manganese dioxide, dilute to 2 l., and store the solution in a glass-stoppered brown bottle for a week before standardizing. Weigh accurately about 0.3 g. of

pure sodium oxalate, and dissolve in about 200 cc. of water. Add 5 cc. of concentrated sulfuric acid, and heat the solution to between 70 and 80°C. Titrate the solution with the potassium permanganate solution, added from a burette with constant stirring, until the pink color produced is discharged but slowly; then add the permanganate drop by drop until the solution remains pink for 2 min. Calculate the normality of the approximately tenth-normal potassium permanganate.

$$\text{Normality of KMnO}_4 = \frac{\text{g. Na}_2\text{C}_2\text{O}_4}{\text{cc. approx. 0.1-N KMnO}_4 \times 0.67}$$

As permanganate solutions change in strength with time and must be restandardized at frequent intervals, it is best not to attempt to adjust the solution to the exact nominal normality but to employ it at the normality found and employ a factor to convert the actual volumes of solution consumed to the corresponding volumes of exactly tenth-normal solution. This factor is the actual normality divided by the nominal normality, or

$$\text{Factor} = \frac{\text{normality found}}{0.1} = \text{normality found} \times 10$$

STANDARD SOLUTIONS FOR IODIMETRY

Preparation of Tenth-normal Potassium Dichromate.—Weigh exactly 4.903 g. of pure potassium dichromate, dissolve in water, and dilute to exactly 1 l. For ordinary work this solution may be taken as exactly tenth-normal without further standardization. If it is desired to standardize the solution, this may be accomplished by titrating a material containing a known quantity of ferrous iron, such as ferrous ammonium sulfate, pure iron wire, or the standard iron ore distributed by the U. S. Bureau of Standards. For the method of titrating the iron with bichromate, consult any textbook on analytical chemistry.

Preparation of Tenth-normal Sodium Thiosulfate.—Weigh roughly about 50 g. of crystalline sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, and dissolve it in about 2 l. of water. Allow the solution to stand several days.

Measure exactly 25.0 cc. of tenth-normal potassium dichromate solution into an Erlenmeyer flask. Add about 100 cc. of water, 5 cc. of concentrated hydrochloric acid, and 10 cc. of a 15-per cent solution of potassium iodide. Allow the solution to stand for about 2 min. Titrate the liberated iodine with the sodium thiosulfate solution, until the brown color of the liberated iodine is nearly discharged, then add about 1 cc. of starch indicator, and continue the titration until the blue color changes to a clear green characteristic of trivalent chromium. Take the first complete disappearance of the blue as the end point, and ignore any return of blue due to air oxidation. Calculate the normality of the sodium thiosulfate solution. Do not adjust the normality, but use the solution as it is, as the solution will probably change in strength slowly for some time and must be restandardized each time that it is used until the normality no longer changes from day to day.

$$\text{Normality of Na}_2\text{S}_2\text{O}_3 = \frac{25}{\text{cc. thiosulfate required} \times 10}$$

$$\text{Factor} = \text{normality found} / 0.1 = \text{normality found} \times 10$$

The volume of thiosulfate solution consumed in a titration, multiplied by this factor, equals the corresponding volume of exactly tenth-normal thiosulfate solution required for the same titration.

Preparation of Tenth-normal Iodine Solution.—This solution is the one used in general iodimetric titrations. For the preparation of special iodine solutions for use in analyzing fats, oils, waxes, and resins, see Chaps. XI and XII.

Weigh 12.7 g. of resublimed iodine, and dissolve in a solution containing 25 g. of pure potassium iodide in 25 cc. water. Transfer to a 1-l. flask, and dilute to the mark. Transfer the solution to a brown bottle, and store it in the dark.

Measure from a burette exactly 25.0 cc. of the iodine solution into an Erlenmeyer flask, dilute to about 200 cc., and titrate with tenth-normal sodium thiosulfate solution until the color has faded to a light straw. Then add about 1 cc. of starch indicator, and continue to add thiosulfate solution, dropwise, until the blue color is completely discharged. Record the volume of thiosulfate required, and ignore any return of the blue color. Calculate the normality and factor of the iodine solution, and use it as of the normality found without further adjustment. Restandardize the solution each day that it is used.

$$\text{Normality of iodine solution} = \frac{\text{cc. 0.1-N Na}_2\text{S}_2\text{O}_3 \text{ solution}}{250}$$

$$\text{Factor of iodine solution} = \text{normality} / 0.1 = \text{normality} \times 10$$

The volume of iodine solution consumed in a titration multiplied by this factor gives the equivalent volume of exactly tenth-normal iodine required for the same titration.

INDICATORS

Methyl Red.—Dissolve 2.5 g. in 500 cc. of 95-per cent alcohol. Test by adding 2 drops to about 100 cc. of freshly distilled water. The color should be clear yellow. Add 1 drop of tenth-normal acid. The color should change to a clear pink.

Methyl Orange.—Dissolve 0.5 g. in 500 cc. of water.

Phenolphthalein.—Dissolve 2.5 g. in 200 cc. of 95-per cent alcohol, and add 250 cc. of water. Add fiftieth-normal sodium hydroxide solution until the solution becomes faintly pink. Then add fiftieth-normal sulfuric acid until the pink color is just discharged.

Starch Solution.—Weigh about 1 g. of arrowroot or potato starch. Mix with water to a thin paste, then add 100 cc. of boiling water. Boil gently for a few seconds. Transfer the hot solution to a small glass-stoppered bottle, cool, and add a drop or two of chloroform as a preservative.

Potassium Chromate.—Dissolve approximately 50 g. of pure potassium chromate in 1 l. of water.

AUTHOR INDEX

A

Adams, F. W., 265
 Alsop, W. K., 59, 412
 Anacker, E., 313
 Anthes, J. F., 62
 Arner, W. J., 366, 370, 414
 Atkin, J., 251, 265
 Atkin, W. R., 39, 42, 59, 214, 217,
 251, 264-266, 313, 316, 318, 349
 Auerbach, M., 413

B

Bailar, J. C., 265
 Balderston, L., 11, 52, 59, 131
 Baldracco, G., 295, 314, 349
 Ball, T. R., 215
 Balland, M., 38
 Bauer, K. H., 413
 Bayliss, W. M., 166
 Beans, H. T., 314, 316
 Beck, A. J., 133
 Beck, C., 84
 Beck, J., Jr., 196
 Belavsky, E., 315
 Bennett, H. G., 7, 59, 265, 314
 Bergmann, M., 110, 131
 Bernard, W., 265
 Bidwell, G. L., 59
 Biilmann, E., 195, 215
 Blackadder, T., 59, 172, 216, 308-
 310, 314, 318
 Blair, C. A., 53
 Blockey, J. R., 59, 349
 Blunt, T. P., 265
 Boidin, A., 163, 166
 Boldyreff, A. W., 218
 Boulanger, H., 84
 Bowker, R. C., 52-54, 59, 132, 134
 Bradley, H., 39, 59, 104, 131

Bradley, W. M., 265
 Breed, R. S., 151
 Breedis, J., 311, 315
 Briggs, R. P., 314
 Brown, R. J., 295, 314
 Bruennich, J. C., 216
 Bruere, A. de la, 314
 Buchanan, E. D., 136, 151
 Buchanan, R. E., 136, 151
 Bumcke, C. G., 413
 Bunker, G. C., 151
 Burton, D., 265, 349, 413

C

Calcott, W. S., 265
 Cameron, D. H., 197, 207, 216, 314
 Camilla, S., 314
 Cantoni, O., 265
 Careggio, L., 62
 Carroll, M. F., 349
 Caste, M., 314
 Caulfield, M. F., 150, 152
 Caunce, A. E., 62
 Chambard, P., 59, 316, 349
 Chamot, E. M., 84
 Charlton, H., 349
 Chaters, W. J., 132
 Churchill, J. B., 34, 59, 62, 131
 Claffin, A., 216, 314
 Clark, W. M., 151, 168, 190, 193,
 200-204, 216
 Clarke, I. D., 10, 59, 60, 63, 132, 133,
 314, 315, 413
 Cohen, A., 39, 59
 Cohen, B., 151, 199, 200
 Coles, A. C., 84
 Colin-Russ, A., 60
 Collins, W. D., 151
 Cornish, R. C., 216
 Craig, T. J. I., 349

Crede, E., 39, 61, 311, 315

Cunningham, T. R., 349

G

D

Dannerth, C. A., 217

Daub, G., 66, 85, 133, 137, 152

Davidson, J., 413

Davis, C. E., 216

Dawson, L. E., 216

Dean, E. W., 60

Deforge, A., 132

Deiter, L. V., 152

De Kruif, P. H., 150, 152

Diener, E. J., 119, 133

Dotterer, W. D., 151

Douglas, W. F., 217

Downing, F. B., 265

Downing, G. V., 110, 133, 315

Drake, N. L., 216

Durand, E. M., 350

E

Endo, S., 151

Englis, D. T., 413

English, F. L., 265

Enna, F. G. A., 60, 265, 350

Escourrou, R., 315

Euler, H. von, 166

Evans, J. V. R., 265

F

Fachini, S., 413

Fales, H. A., 190, 216

Falk, I. S., 150, 152

Falk, K. G., 166

Fasol, T., 216

Faust, T. A., 315, 413

Favre, L., 318

Ferguson, W. C., 332, 335, 429

Fleming, J. W., 58, 137

Foot, H. W., 265

Foster, S. B., 351

Frey, R. W., 10, 23, 59, 63, 132, 133,
314, 315

Frieden, A., 48, 63, 318

Fudge, J. F., 217

Fuwa, T., 134

Gage, H. P., 84

Gage, S. H., 84

Gallun, A. F., Jr., 111, 115, 133, 255,
266, 310, 319

Gallun, E. A., 11

Garland, C. E., 314

Gayley, C. T., 62, 132

Geib, M. N. V., 131

Gerlach, 339

Germuth, F. G., 349

Gerngross, O., 60, 315

Gerssen, N. J., 132

Gilbert, D. E., 134

Gillet, M., 413

Girard, A., 315

Gnam, H., 382, 413, 438, 472

Goldenburg, A. M., 60

Granger, F. S., 216

Grasser, G., 130, 132, 349

Greeves, W. S., 117, 132

Griffin, R. C., 265, 349, 413

Guettler, R. O., 133

Gustavson, K. H., 45, 60

H

Han, J. E. S., 349

Hanausek, T. F., 84

Handley, E. G., 132

Harden, W. C., 216

Harrison, A. P., 62

Harrison, J. P. B., 349

Hart, R. W., 132-134, 413

Harvey, A., 60, 315, 349, 414

Haslam, J. K., 265

Haslam, R. T., 265

Hassan, K., 318

Hayes, H., 265

Henrich, R. G., 17, 20, 213, 243, 373,
387, 395

Hepburn, J. R. I., 349

Herbig, W., 414

Hertwig, R., 414

Hey, A. M., 60

Highberger, J. H., 251, 253-254, 265

Hill, H. W., 151

Hind, H. L., 84

Hirsch, M., 132
 Hollander, C. S., 166
 Hou, Te-Pang, 60
 Hough, A. T., 315
 Huc, P., 132
 Hudson, F., 60
 Hugonin, G., 216, 315
 Hunt, M. G., 63

I

Innes, R. F., 39, 42, 43, 60, 61, 350

J

Jablonski, L., 61, 132
 Jaervinen, K. K., 350
 Jalade, E., 61, 132
 Jamet, A., 315, 316
 Jamieson, G. S., 414
 Jaramillo, G., 61
 Jarrell, T. D., 61, 63, 266
 Jenkins, L. J., 23, 60
 Jones, H. M., 151
 Joslin, H. M., 23, 60

K

Kanhauser, F., 350
 Kaye, M., 84
 Kean, R. H., 265
 Kelly, M. W., 25, 61, 295, 313, 318, 351
 Kendall, A. I., 152
 Kenny, W. R., 217
 Kern, E. J., 32, 57, 63, 111, 125, 133, 174, 218, 268, 288, 290-295, 315, 319, 390, 414
 Kerr, R. H., 414
 Kinyoun, J. J., 152
 Klaber, W., 350
 Knowles, G. E., 315
 Knowles, P. E., 265
 Koehler, L., 216
 Koenig, J. W., 315
 Kohn, S., 39, 61, 311, 315
 Kubelka, V., 166, 216, 265, 315, 350
 Kuhn, R., 166
 Kung, A. H., 217
 Kuntzel, A., 85

L

LaMer, V. K., 195, 217
 Lang, G., 414
 Lange, A. R., 414
 Last, E., 414
 Latshaw, W. L., 61
 Lauffmann, R., 61, 316, 350
 Lee, A. B., 66, 85
 Leinbach, L. R., 60, 132, 133
 Lepage, G., 63
 Levi, L. E., 61, 316, 350, 414
 Levine, M., 152
 Lines, G. O., 49, 63, 103, 104, 107, 134
 Little, E., 61, 314, 316, 350
 Lloyd, D. J., 84
 Loeb, J., 149, 152
 Long, J. S., 453, 472
 Longbottom, H. L., 316
 Lubs, H. A., 151, 199
 Ludewig, S., 110, 131
 Lund, H., 216

M

MacIntire, W. H., 266
 Maljean, 38
 Mallory, F. B., 73, 85
 Manuel, E. V., 316, 350
 Marshall, C. E., 152
 Marshall, F. F., 316
 Mathews, R. R., 414
 McCandlish, D., 132, 266, 316, 350
 McCrumb, F. R., 217
 McHenry, M. J., 217
 McKay, A. T., 104, 131
 McLaughlin, G. D., 66, 85
 McNeill, T. R., 349
 McNicoll, D., 414
 Meerbott, P. B., 415
 Memmen, F., 167
 Merrill, H. B., 31, 45, 55, 61, 137, 167, 316
 Messe, W., 350
 Meunier, L., 316
 Mezey, E., 316
 Mills, V. C., 413
 Moore, E. K., 251, 253-254, 265

Morgenstein, V., 217
 Mosser, T. J., 61
 Mudd, J. S., 61
 Mudge, W. A., 190, 216
 Mueller, E., 350

N

Nelson, J. M., 216
 Niedercorn, J. G., 45, 61
 Nihoul, E., 132
 Northrop, J. H., 150, 152, 163, 164,
 166
 Noyes, H. A., 152

O

Oberfell, C. R., 61, 414
 O'Flaherty, F., 66, 85
 Olson, R. M., 57
 Oppenheimer, O., 166
 Orthmann, A. C., 7, 54, 61, 110, 132,
 316, 350, 366, 370, 414

P

r, J., 316
 Page, R. O., 31-33, 62, 268
 Palmer, J. C., 414
 Palmer, W. E., 265
 Parker, H. C., 217
 Parker, J. G., 316
 Parsons, L. B., 217
 Parsons, T. R., 195, 217
 Pavlovitch, P., 132
 Pebody, P. L., 61
 Phillips, R. O., 317
 Pickard, R. H., 62
 Pickering, J. E., 350
 Pickles, J. E., 266
 Pierce, W. H., 217
 Pilgrim, J. A., 317
 Pleass, W. B., 197, 217
 Pollak, L., 317
 Poncet, J., 63
 Popoff, S., 217
 Porter, R. E., 53, 132, 317
 Powarnin, G., 132
 Priest, G. W., 414

Procter, H. R., 37, 62, 266, 308, 317,
 350, 414, 416, 472

Q

Quarek, R., 45, 61

R

Randles, W. B., 84
 Reed, E. O., 60
 Reed, H. C., 34, 62, 315, 317
 Rehbein, G., 62
 Reisnek, A., 132
 Reithof, O., 62
 Riess, C., 317, 393, 415
 Riffenburg, H. B., 151
 Rodman, G. H., 85
 Rogers, A., 132
 Rogers, J. S., 62, 266, 317
 Rose, R. E., 417
 Rosser, L., 217

S

Salisbury, H. M., 216
 Sander, A., 62
 Sandor, G., 315
 Sargent, E., 61
 Scales, F. M., 62
 Schacherl, R., 393, 394, 415
 Schaefer, W. E., 60
 Schell, E., 318
 Schiaparelli, C., 62
 Schindler, W., 393, 394, 415
 Schlegel, J. W., 217
 Schneider, J., 167
 Schollenburger, C. J., 217
 Schorlemmer, K., 350
 Schuber, H., 151
 Schultz, G. W., 62, 318, 414
 Scott, W. W., 266, 350, 414, 473
 Seel, E., 62
 Seltzer, J. M., 62
 Seshachalam, K., 318
 Seymour-Jones, A., 85
 Seymour-Jones, F. L., 167
 Shaw, R. G. F., 413
 Shaw, W. M., 266

Sheard, L., 318
 Shearer, R., 216
 Sheppard, S. E., 85
 Simonecini, E., 318
 Small, F. H., 62
 Smetkin, A., 132
 Smith, C., 350
 Smith, H. M., 152
 Smoot, C. C., III, 318
 Smull, J. G., 472
 Snow, R. D., 217
 Sorber, D. G., 414
 Spiers, C. M., 131
 Sprague, F. O., 133
 Stacey, L. E., 62
 Stadler, O., 415
 Stanislaus, I. V. S., 415
 Stark, D. D., 61
 Sterling, W. F., 59
 Stiasny, E., 167, 217, 266, 295, 318,
 351, 387, 393, 415
 Stueber, A. H., 217
 Sutermeister, E., 473
 Suzuki, K., 252, 266

T

Talbot, H. P., 332
 Terrasse, G. L., 62
 Terrell, J. T., 317
 Terroine, E. F., 63
 Thomas, A. W., 38, 44-45, 48, 63,
 167, 170, 217, 295, 313, 318, 323,
 351
 Thompson, F. C., 39, 42, 59, 214,
 217, 252, 266, 313, 318, 349
 Thornton, W. M., Jr., 473
 Thuau, U. J., 133, 318
 Trivelli, A. P. H., 85
 Turley, H. G., 85
 Turnbull, A., 318

U

Underwood, J. E., 266

V

Van der Hoeven, C., 63, 218
 Van der Waerden, H., 133, 415

Van Heurn, F. C., 351
 Van Urk, H. W., 218
 Varo, W., 109
 Veitch, F. P., 63, 133, 266
 Vlcek, A., 167
 Vollmar, C. J., 145-50, 152

W

Wagner, J., 63, 166, 216, 316
 Waldschmidt-Leitz, E., 167
 Walker, A. W., 152
 Wallace, E. L., 196
 Ware, A. H., 318
 Watson, J. C., 265
 Welwart, N., 415
 Whipple, G. C., 85, 152
 Whitmore, L. M., 110, 133, 134
 Whittaker, H. A., 152
 Wightman, E. P., 85
 Willard, H. H., 218
 Williams, H. E., 318
 Willstaetter, R., 167
 Wilson, J. A., 32, 49, 63, 65, 85,
 103, 104, 107-109, 111, 115,
 118-128, 133-134, 137, 145-150,
 152, 160, 167, 174, 218, 255,
 266, 268, 288, 290-295, 310,
 311, 318, 319, 351, 415, 473
 Wilson, R. E., 134
 Wilson, S. P., 471, 473
 Winandy, P., 134
 Winch, L., 317
 Winslow, C. E., 150, 152
 Wohlge-muth, J., 167
 Wolf, K., 218
 Wolff, H., 400
 Woodroffe, D., 63, 64, 134, 351
 Wormeley, P. L., 134
 Worswick, B., 104, 131
 Wright, J. H., 73, 85
 Wright, R., 64
 Wuensch, 38, 41
 Wyler, J. A., 266

Y

Yokum, J. H., 297

SUBJECT INDEX

Aberration, 77-78

Acetic acid, analysis of, 427

determination of, in acetic acid,
427

in formic acid, 424

melting point of, 441

reagent, for iodine value, 441

uses in tannery, 423

Acetyl value, 379

Acid, mineral, in moellon dégras, 384

in vegetable-tanned leather, 37-
44

detection of excessive, 39-43

determination, by Procter-
Searle method, 40-41

errors in existing methods,
37-38

total, determination of, in alu-
minum sulfate, 331

in chrome liquors, 326

in chromium chloride, 325

in chromium sulfate, 323

in drenches, 264

in formaldehyde, 446

in hydrochloric acid, 335

in pickle liquors, 339

by potentiometric titration,
168, 215

in sodium sulfate, 225

in solvents, 463

in sulfuric acid, 331

in tan liquors, by A.L.C.A.
method, 277

by potentiometric method,
300

(See also Acidity.)

volatile, determination of, in

drenches, 264

in lactic acid, 425-426

Acid dyes, identification of, 416

Acid number, 375

of fatty acids of soap, 406

of linseed oil, 450

Acidimetry, 169

solutions for, preparation, 475-479

Acidity, of aluminum sulfate, 330

of casein, 433

of chrome liquors, 325-326

of chromium salts, 324-325

in leather, 46-47

effective, 170

of solvents, 463

of syntans, 313

total, of solutions, 168, 215

Acidity potential (Blackadder scale),
172

Acidity value, of leather, 42

Acids, deliming with, 257

fatty (see Fatty acids).

organic, uses in tannery, 423

pickling with, 321, 338

resistance of leather to, 118-119

standard solutions, preparation,
475-479

(See also individual acids.)

Air bubble method for viscosity, 365

Albumin, determination of, in egg

yolk, 411

soluble, in commercial albu-
mins, 436

(See also Blood albumin.)

egg (see Egg albumin).

Alcohol, denatured, for nitrocellulose

testing, 458

Alcohols, higher, of waxes, 437-438

as lacquer solvents, 456

Aldehydes, in leather, 48

Algin, 430, 446

Alkali, caustic, determination of, in

borax, 346

- Alkali, caustic, determination of, in
lime liquors, 251
in soap, 403
in sodium sulfite, 342
(*See also* sodium hydroxide.)
combined, determination of, in
soap, 407
in sulfonated oil, 391
excess, determination of, in sodium
sulfide, 245
total, determination of, in calcium
chloride, 249
in fat liquors, 412
in fillers of soap, 404
in soap, 401
in solvents, 463
in sulfonated oil, 388
in tan liquor ash, 298
- Alkalinity, determination of, of fat
liquors, 396
pH value and, 171
of soaps, 396, 401
(*See also* Alkali.)
- Alum (*see* Aluminum sulfate).
- Aluminum, determination of, in
aluminum sulfate, 330
in chromic sulfate, 323
in leather, 17, 21-23
in lime, 237
in sodium chloride, 222
in tan liquors and extracts, 298
in water, 228
separation of, from iron, 221
- Aluminum compounds, in chrome
tanning materials, 321
tanning with, 320
- Aluminum sulfate, analysis of, 329
in coloring, 320, 329
composition of, 329
denaturant for salt, 220
in tanning, 320, 329
- American Chemical Society, meth-
ods, for analysis of soap, 397,
400, 402-403, 406
- American Leather Chemists Associa-
tion, methods, for analysis,
of chrome liquors, 326
of fats, oils, and greases, 358,
359, 373, 376
- American Leather Chemists Associa-
tion, methods, for analysis,
of lactic acid, 425-427
of leather, 13-49
of moellon dégras, 384
of sulfonated oil, 386-395
of tanning materials, 273-285
for sampling, leather, 9-11
tanning materials, 269-273
- American Society for Testing Mate-
rials, methods, for cloud point,
366-370
for distillation, 464-470
for lime (analysis of), 236-241
for linseed oil, 448-453
for melting point, of paraffin,
381-382
for nitrocellulose, testing of, 458
for oils, testing of, 360-370
for paraffin, melting point of,
381-382
for pour point, 366-370
for shellac, testing of, 439-446
for solvents and diluents, test-
ing of, 461-470
for specific gravity of fats solid
at room temperature, 357
for viscosity, 360-365
- Amines, determination of, in lime
liquors, 253
- Ammonia, aqua, analysis of, 428-429
composition of, 428
specific gravity tables, 428
determination of, in ammonium
chloride, 258
by direct titration, 429
by distillation, 389, 436
in lime liquors, 252-254
in sulfonated oils, 389
by vacuum distillation, 252
(*See also* Ammonium salts.)
- Ammonium chloride, analysis of, 258
- Ammonium hydroxide (*see* Ammo-
nia, aqua).
- Ammonium molybdate, reagent,
preparation of, 432
- Ammonium oxalate, standard, prep-
aration of, 230

- Ammonium salts, analysis of, 258-259
as bating agents, 257
determination of, in albumins, 436
in bate liquors, 263
in dry bates, 262
Ammonium sulfate, analysis of, 259
Antimony, determination of, in potassium antimonyl tartrate, 422
test for, in leather, 15
Antiseptics, prevention of bacterial damage by, 137
for soaking, 226
Arsenic, determination of, in arsenic sulfide, 247
Arsenic sulfide, analysis of, 247-248
Arsenious acid, standard, preparation of, 231
Asbestos, for crucibles, purification, 37
Ash (*see* Mineral matter).
Association of Official Agricultural Chemists, methods for borates, 409-410
for iodine value, 377-378
for melting point, 358
- B**
- Bacteria, 135-152
in bate liquors, 136, 263
classification of, 135-136
colloidal behavior of, 149
counting, 138-150
damage to skins by, 136-137
pH value and, 137-138
prevention of, 137
description of, 135-136
pure cultures, 150-151
in soak liquors, 144-149, 232
Bacterial counts, 135-152
of bate liquors, 136, 263
effect of salts on, 145
effect of temperature on, 144
official methods for making, 138-144
apparatus for, 138
counting, 1-44
Bacterial counts, official methods for making, culture media, 139-142
dilutions, 143
incubation, 144
plating, 143
samples, 143
of soak liquors, 144, 233
Barium carbonate, determination of, in barium sulfide, 246
Barium sulfate, determination of, in barium sulfide, 246
in leather, 15-16, 18, 21-23
in sodium chloride, 221
Barium sulfide, analysis of, 245-246
Barkometer, 296
temperature correction table, 296
Barks, tanniferous, extraction of, 274
sampling, 271, 280
tannin content of sundry, 311
Basic dyes, identification of, 416
Basicity of chrome salts, in leather, 47
in liquors, 326
Bate liquors, 257, 262-264
analysis of, 262-264
bacteria in, 136, 263
pH value of, 262
Bates, commercial, analysis of, 261
manufacture of, 259-260
Bating, 257
Bating materials, 257-264
Beamhouse, 219
liquors and materials, analysis of, 219-266
operation, 219
Beef tallow, constants of, 354
used in stuffing, 26
Beeswax, constants of, 437
used in finishing, 430
Benzene, for freezing-point determination, 453
Bicarbonates, determination of in water, 229
titration in presence of carbonates, 344
(*See also* Sodium bicarbonate.)
Binders, in finishes, 430
Bismarck brown, stain, 72

- Bleaching powder (*see* Calcium hypochlorite).
- Blood albumin, analysis of, 434-437
composition of, 435
- Boil test, for chrome leather, 118
- Bone fat, constants of, 354
- Borate buffers, 201-204, 207
- Borates, detection of, 409
determination of, in borax, 346
in egg yolk, 409-410
- Borax (*see* Sodium borate).
- Boric acid method for nitrogen, 25-26
- Break of leather, 128-130
- Breaking point of leather (*see* Tensile strength).
- Brom chlor phenol blue, indicator, 199
- Brom cresol green, indicator, 199, 200, 211
- Brom cresol purple, indicator, 199, 200, 211
- Brom phenol blue, indicator, 199, 200, 211
- Brom phenol red, indicator, 199, 200, 211
- Brom thymol blue, indicator, 199, 200, 211
- Buffers, 193, 201-204
for determining pH by titration, 207
for hydrogen-ion colorimeter, 210
preparation of standard, 201-204
- Butanol, analysis of (*see* Solvents).
specifications for, 462
- Butyl acetate, analysis of (*see* Solvents).
specifications for, 462
- Butylalcohol (*see* Butanol).
- C**
- Calcium, determination of, 17, 237
as calcium sulfate, 432
in casein, 432
in lactic acid, 425
in lime, 237
in leather, 17
by permanganate method, 237
- Calcium, determination of, in sodium chloride, 222
in titanium potassium oxalate, 419
qualitative test for, 422
- Calcium chloride, analysis of, 249
as curing agent, 219
in lime liquors, function of, 234
- Calcium chloride solution, acid, reagent, preparation of, 450
- Calcium hydroxide, determination of, in lime, 239
in lime liquors, 251
(*See also* Lime.)
- Calcium hypochlorite, analysis of, 232
antiseptic in soaking, 226
- Calcium oxide (*see* Calcium hydroxide; Lime).
- Calcium sulfhydrate, analysis of, 246
formed from arsenic sulfide and lime, 247
- Calcium sulfide, 246
- Calomel electrode, 173-178, 189-190
construction of, 175, 177-178
E.M.F. of, 189-190
affected by KCl concentration, 177, 189
affected by temperature, 190-192
- Canaigre, analytical charge, 285
- Candelilla wax, constants of, 437
- used in finishes, 430
- Candles, filter, 287
- Capillary method for melting point, 358
- Capillary viscosimeter, 459
- Carbol-xylene, clearing agent, 67
- Carbon, elementary, determination of, in barium sulfide, 246
impurity in chromium sulfate, 321
- Carbon disulfide, as fat solvent, 26-31
- Carbon tetrachloride, as fat solvent, 26-31
- Carbonates, determination of, by evolution method, 238
in lime, 238

- Carbonates, determination of, in
sodium hydroxide, 248
by titration, in presence of
bicarbonates, 227, 344
in presence of hydroxide,
248, 277, 344
in water, 277
(See also Sodium carbonate.)
- Carnauba wax, analysis of, 438-439
constants of, 437, 438
grades, 438
used in finishes, 430
- Casein, analysis of, 431-434
enzyme action on, 163-164
general substrate for measuring
enzyme activity, 153
used in finishes, 430
- Castile soap, composition of, 397
reagent for hardness of water, 230
- Castor oil, constants of, 354
hydroxyl value of, 379
sulfonated, 26, 386
- Caustic soda (see Sodium hydroxide).
- Chestnut extract, analytical charge,
285
composition of, 312
sampling, 271
- Chestnut wood, analytical charge,
285
- Chlor phenol red, indicator, 199, 200
- Chloride, acid, in chromic chloride,
325
- Chlorides, determination of, in
chrome leather, 47-48
in chromium chloride, 325
in chromium sulfate, 324
in lime, 238
in lime liquors, 255
by Mohr method, 223
in soaks, 234
in sodium chloride, 223
in tan liquors, 298
by Volhard method, 255
in water, 227
effect of, on bacterial counts,
145-150
neutral (see Sodium chloride).
(See also Chlorine.)
- Chlorine, antiseptic in soaking, 226
available, in bleaching powder,
231
effect of, on bacterial count of
water, 145
total, determination of, in albu-
mins, 436
in casein, 433
in tanning extracts, 299
in vulcanized oils, 455
- Chloroform, as fat solvent, 26-31
- Chlorplatinite method for potas-
sium, 421-422
- Cholesterol, in skin fat, 28
- Chrome alum, analysis of, 321
for treating hide powder, 275, 280
- Chrome tanning, 320
- Chrome tanning liquors, 325-327
analysis of, 325-327
composition of, 325
neutralization of, 320
pH value of, 327
- Chrome tanning materials, 320-351
manufacture of, 320-321
(See also Chromium com-
pounds.)
- Chromic acid, determination of, in
sodium dichromate, 328
- Chromic salts, in chrome tanning,
320
- Chromium, determination of, in
chrome liquors, 326
in chromium sulfate, 322
in leather, 20-23
in sodium dichromate, 328
- Chromium chloride, 325
- Chromium compounds, analysis of,
320-329
basicity of, in chrome liquors, 326
in leather, 46-47
used for tanning, 320
- Chromium sulfate, basic, acidity of,
324
analysis of, 321-324
composition of, 321
manufacture of, 320-321
tanning with, 320
- Clearing agents, 67
- Cloud point of oils, 366-370

- Cochineal, indicator, preparation of, 25
- Coconut oil, constants of, 354
- Cod liver oil, constants of, 354, 356
sulfonated, 26, 386
used in oiling leather, 26
- Collagen (*see* Hide substance; Nitrogen).
- Collodion (*see* Nitrocellulose).
- Color, of carnauba wax, 438
of lactic acid, 425
of leather, effect on temperature, 119
of linseed oil, raw, 452
of shellac, 446
of solvents, 463
of tanning materials, 300, 307-310
- Colorimeter, Blackadder, 307-310
hydrogen-ion, 208-214
Lovibond, 300
- Colorimetric method for pH value (*see* Indicator method).
- Coloring materials, analysis, 415-429
dyes, 416-418
mordants, 418
strikers, 418
- Coloring matter, in leather, 48
- Comparator, 204-207
roulette, 205
- Condenser, for analytical distillation, 465
sub-stage, of microscope, 74, 82
- Conductance method, for acid sulfate in chromium compounds, 323
- Copal, in rosin, 443-444
- Copper corrosion test, for solvents, 464, 472
- Corn oil, constants of, 354
- Corrosive sublimate (*see* Mercuric chloride).
- Cottonseed oil, constants of, 354, 356
- Counting bacteria, 144
- Cracking of leather grain, 97
- Cresol phthalein, indicator, 199
- Cresol red, indicator, 199, 200, 211
- Culture media, 139-142
- Cultures, pure, 150-151
- Curing, 219
bacterial damage during, 137
- Cutch extract, analytical charge, 285
composition of, 312
- D
- Dégras (*see* Moellon).
- Dégras-former (*see* Fatty acids, oxidized).
- Dehydration of skin for microscopic study, 66
- Deliming, 257
- Density (*see* Specific gravity).
- Dextrin, 430
- Dextrose (*see* Glucose).
- Difference figure, 39, 43
- Diluents, for lacquers, 456, 461-470
- Dilutions, for bacterial counts, 143
of tan liquors for analysis, 276
of tannin extracts for analysis, 285, 292
- Dimensional changes of leather with relative humidity, 111-117
- Direct dyes, identification of, 416
- Dishes, for tannin analysis, 277, 278
- Dissociation, electrolytic, 169-170
- Distillation, of ammonia, free, 436
in Kjeldahl method, 24-25
from lime liquors, 252-253
of naphtha from vulcanized oils, 455
of solvents, 463, 464-470
of volatile acids, 264
- Divi divi, analytical charge, 285
composition of, 312
- Dolphin oil, constants of, 354
- Drenches, 258, 264
- Drying time, of boiled linseed oil, 453
- Dyes, 416-418
for culture media, 142
in finishes, 430
- E
- Egg yolk, analysis of, 408-412
composition of, 407
in fat liquoring, 26, 352

- Elastin, enzyme action on, 159-160
- Electrodes (*see* Hydrogen electrode, etc.).
- Electro-motive force, of calomel electrode, 190
- affected by potassium chloride concentration, 178, 189
- by pressure, 190
- by temperature, 189-190
- origin of, 173
- relation to pH value, with glass electrode, 196-197
- with hydrogen electrode, 173, 189-193
- with quinhydrone electrode, 195
- of standard cell, 180-183
- Empirical methods, limitations of, 1
- Emulsions, sulfonated oil, 385
- stability test for, 395
- Enzyme activity, 153-167
- of dry bates, 158, 262
- measurement of, principles, 153-156
- methods for measuring, on casein, 163-164
- on collagen, 160-162
- on elastin, 159-160
- on keratose, 157-159
- on oils, 165-166, 256
- of pancreatin, 158, 259
- of trypsin, 153-167
- Enzymes, activity of (*see* Enzyme activity).
- bating action, 257
- secreted by bacteria, 136
- unhairing action, 154, 234
- Epsom salt (*see* Magnesium sulfate).
- Erlicki's fluid, 66
- Ester value of solvents, 463-464
- Esters, as solvents, 456
- Ether, ethyl, as fat solvent, 26-31
- Ethyl acetate, analysis of (*see* Solvents).
- for nitrocellulose testing, 458
- specifications for, 462
- Evaporation, of tannin solutions, 277, 278, 286
- Evaporator-drier, 277
- Extractor, for tanning materials, 274, 279, 285, 293
- for water-soluble matter in leather, 34, 35
- Extracts, tannin, analysis of, 274-276, 282-285, 290-295, 297
- chlorine in, 299
- color of, 300, 307-310
- composition of, 310, 312
- glucose in, 299-307
- mineral matter in, 297-298
- pH value of, 300
- quantities taken for analytical solution, 285, 292
- sampling of, 269-273, 281
- solution of, for analysis, 274-275, 282, 292
- specific gravity of, 296
- sulfur in, 299
- (*See also* Tanning materials.)
- Eye-piece, 74, 78-82
- micrometer, 79-81
- compensating, 81
- flat-field, 82
- F**
- Fat, determination of, neutral, in sulfonated oil, 394
- total, in leather, 26-31
- effect of solvent, 3, 26-30
- in casein, 433
- in egg yolk, 410
- in pancreatin, 260
- in soap, 398
- in sulfonated oil, 392
- unsaponified, in soap, 398
- Fat content of leather, effect of, on porosity, 108-109
- on resilience, 126
- materials included as, 26
- Fat liquoring, 352
- alkalinity and, 396
- soap in, 396
- with sulfonated oil, 385
- Fat liquoring materials, enumeration of, 352
- Fat liquors, alkalinity of, 396
- analysis of, 412
- stability of, 396

- Fats, constants of, 354-356
from egg yolk, analysis of, 411
from leather, analysis of, 31
melting point of, 358-359
and oils, analysis of, for acetyl value, 379
for cloud point, 366-371
for free fatty acids, 375-376
for iodine value, 376-378
for matter insoluble in benzene, 371-372
for Maumené value, 380
for melting point, 358-359
for mineral matter, 371
for oxidized fatty acids, 374-375
for pour point, 366-371
for saponification value, 378-379
for specific gravity, 356-357
for unoxidized fatty acids, 374-375
for unsaponifiable matter, 372-374
for viscosity, 359-365
for water, 371
solid, specific gravity of, 357
used in fat liquoring, stuffing, and oiling, 26
- Fatty acids, combined, in sulfonated oils, 388-389
free, determination of, in fats, 375
in linseed oil, 450
in moellon, 384
in soap, 400
in sulfonated oil, 388-389, 394
formed by enzyme action, 165, 375
in leather, 366
melting point of, significance, 366
oxidized, in fats, determination of, 375
in moellon, dégras-former, 382
determination of, 384
in vulcanized oils, 454
of soaps, determination of as anhydrides, 399
examination of, 405
importance of, 395-396
- Fatty acids, in sulfonated oil, 394
unoxidized, determination of, 374-375
examination of, 374-375
Fehling's solution, preparation, 36
Ferric chloride test for non-tannin, 293
sensitivity of, 295
Fig soap, composition of, 397
Fillers, in soap, alkalinity of, 404
determination of, 403
matter insoluble in water in, 404
Film test for nitrocellulose, 461
Filter cloth, for tannin determination, 293
Filter paper, for tannin analysis, 275, 279, 287
Filtration of tannin solutions, 275, 284, 287
with candle, 287
Finishes, 430-431
analysis, 447
Finishing materials, analysis, 430-448
classification of, 430
effect of, on break of leather, 129
on porosity of leather, 107, 109
Fixative, Mayer's, 71
Fixing, 66
Flask, Engler, 464
Foots, in linseed oil, 453
Formaldehyde, analysis of, 446-447
in finishes, 430, 446
fixing agent, 66
Formic acid, analysis of, 423-425
disinfecting with, 219
soaking with, 226
specific gravity table, 424
Freezing-point depression, control method for boiling linseed oil, 453-454
Fruits, tanniferous, sampling of, 271, 280
Furfural, in acetic acid, 427
Fusion mixture, for chrome leather ash, 21-22
- G
- Galls, sampling of, 271
Galvanometer, 181, 184

- Gambier extract, analytical charge, 285
for Wilson-Kern method, 292
composition of, 312
sampling of, 271
- Gelatin-salt test for tannin, 290, 293
reagent, preparation, 280, 292
sensitivity of, 295
- Gelatin solution, for total acid determination, 277
- Glass electrode, 197
- Glauber's salt (*see* Sodium sulfate).
- Glucose, in chrome salt manufacture, 321
determination of, in leather, 35-37
in tannin extracts, 299-300
Munson and Walker's tables for, 301-307
reducing agent, 321
- Gooch crucibles, for glucose determination, preparation, 37
- Gravimeter, 296, 357
- Grease, hard, examination of, for free fatty acids, 376
for melting point, 358
for unsaponifiable matter, 373
- Grinding tanning materials, 273, 280
- Gums, 430, 446

H

- Halphen-Hicks reagent for rosin, 443
- Hanus method for iodine value, 376-378
- Hardness of water, determination, 230
- Heat, resistance of leather to, 118
- Heating, loss on, of linseed oil, 452
- Hematin solution, for total acid determination, 277
- Hemlock bark, analytical charge, 285
- Hemlock extract, analytical charge, 285
for Wilson-Kern method, 292
composition of, 312
- Herring oil, constants of, 354
- Hide powder, method for tannin, 267
- Hide powder, purification of, 161
for tannin analysis, chroming, 275, 283
purification (Wilson-Kern method), 292
quantity taken for detannization, 277
variations in, 288
water content, 276, 289
- Hide substance, determination of (*see* Nitrogen).
enzyme action on, 136, 160-162
nitrogen content of, 1, 25
- Hides (*see* Skins).
- Hydrocarbons, as diluents for lacquer, 456
as stuffing and oiling materials, 26
- Hydrochloric acid, analysis of, 335-338
deliming with, 257
determination of, in chrome leather, 47
in chromic chloride, 325
in hydrochloric acid, 335
in sulfuric acid, 334
specific gravity table, 335-337
standard, preparation of, 475-479
- Hydrogen, for pH measurements, 178
- Hydrogen electrode, compared to indicator method for pH, 214
construction, 174
determining pH value with, 173-194
limitations of, 193, 214, 313
platinizing, 175-177
theory of, 173-174
titrations with, 169, 215
of acids, 215, 300
of phosphates, 347-348
of tan liquors, 300
useless with syntans, 313
- Hydrogen-ion concentration, definition of, 169
effect of, on indicators, 197
expression of, methods, 170-172
measurement of, 168-218
and pH value, 170-172
(*See also* pH value.)

Hydrogen ions, 168-171
Hydrolysis, of chromic salts, 323
 in leather, 44
 of hide-tannin compound, 31-33, 291-292
Hydrometer method for specific gravity, 331
Hydroxides, determination of, in water, 229
 (See also Alkali, caustic)
Hydroxyl ions, 168-171, 197
Hydroxyl value of fats (see Acetyl value).
Hypo (see Sodium thiosulfate).

I

Imbedding, 66
Incubation of plates for bacterial counts, 144
Indicator method for pH value, choice of indicators, 198-200
 colorimeter method, 208-214
 calculations, 212
 comparator, 204
 compared to potentiometric method, 214
 in highly colored solutions, 214
 preparation of indicators, 200-201
 procedure with comparator, 205-207
 theory of, 197-198
 titration method (Cameron), 207
 standards for comparison, buffer solutions, 201-204
 glass standards, 207
Indicators, for pH measurements, with colorimeter, 210
 with comparator, 197-201
 theory of, 197
 for titrations, preparation of, 481
Insoluble matter (see Matter in-soluble in alcohol, water, etc.).
International method for tannin analysis, 278-285
Iodimetry, standard solutions for, 480-481
Iodine solutions, standard, for

 Iodine solutions, standard, for
 Hanus method, 376-378
 for Wijs method, 441-442
Iodine value, of fats and oils, 376-378
 Hanus method for, 376-378
 of linseed oil, 451-452
 of shellac, 441-442
 Wijs method for, 441-442, 451-452
Ionic theory, 168-170
 applied to indicators, 197
Irish moss, 430, 446
Iron, determination of, in chromium compounds, 322
 by colorimetric method, 222, 228
 in hydrochloric acid, 337
 in lactic acid, 425
 in leather, 16-17, 21-23
 in lime, 236
 in sodium chloride, 221
 in sodium sulfide, 245
 in tanning materials, 298
 in titanium potassium oxalate, 419
 in water, 228
 separation of, from aluminum, 22, 222, 236
Iron compounds, in chrome tanning compounds, 321
 tanning with, 320
Iron sulfide, in barium sulfide, 246
 in sodium sulfide, 241, 245

J

Japan wax, constants of, 437
 used in finishes, 430

K

Kaolin, for tannin analysis, 275, 279
Keratose, enzyme action on, measurement, 157-159
 as general substrate for measuring enzyme activity, 154
 preparation of, 157
Ketones, as solvents, 456
Kjeldahl method for nitrogen, 23-26

Knife, microtome, 68-70
Koch extractor, 279
Koettsdorfer number (*see* Saponification value).

L

- Lacquers, analysis of, 471-472
 compounding of, 456-457
 nitrocellulose (*see* Nitrocellulose).
Lactic acid, analysis of, 425-427
 anhydride, 426-427
 deliming with, 257
 determination, in drenches, 264
 free, 426-427
 use in tannery, 423
La Motte purple, indicator, 199
La Motte sulfo orange, 199
La Motte violet, 199
Larch extract, analytical charge
 (Wilson-Kern method), 292
 composition, 312
Lard oil, constants of, 354
Lead, determination of, in boiled
 linseed oil, 453
Leather, analysis (chemical) of,
 7-64
 for acidity of chrome salt, 46-47
 for aluminum, in chrome leather,
 20-23
 in vegetable leather, 17
 for antimony, 15
 for ash, 13-15
 for barium sulfate, 15-16, 18,
 21-23
 for calcium, 17
 for chlorides, 47-48
 for chromium, 20-23
 for collagen, 23-26
 for collodion, 49
 for combined tannin, 48-49
 for fat, 3, 26-31
 for glucose, 35-37
 for hide substance, 1, 23-26
 for hydrochloric acid, 47-48
 for iron, in chrome leather,
 21-23
 in vegetable leather, 16-17
 for magnesium, 17-20
Leather, analysis (chemical) of, for
 mineral acid, combined, 44
 in vegetable tanned leather,
 37-44
 for mineral matter, 13-15
 soluble and insoluble, 14-15,
 35
 for neutral chloride, 47-48
 for nitrogen, 1, 23-26
 for silica, 16
 for sulfate, in chrome leather,
 44-46
 for sulfur, total, in vegetable
 leather, 41-42
 for titanium, 15, 18
 for water, 11-13
 for water-soluble matter, 3,
 31-35
 chrome tanning of, 320
 coloring of, 416
 composition of (examples), 49-59
 effect of location, 55-59
 fat liquoring of, 26, 352
 finishing of, 430
 loading materials in, 33
 microscopic examination of, 65-85
 imbedding, 66
 sampling for, 65
 sectioning, 71
 staining, 71
 physical properties of, 86-134
 break, 128-130
 cracking of grain, 99
 dimensional changes with relative
 humidity, 111-117
 permeability, to gases, 107-110
 to water, liquid, 110
 to water vapor, 102-106
 porosity, 107-110
 resilience, 124-128
 resistance, to acids, 118-119
 to heat, 118
 to stretching, 86-97
 to tearing, 97-99
 specific gravity, 11, 130-131
 stretching, resistance to, 86-97
 cracking of grain and, 99
 recovery after, 97

- Leather, physical properties of, tearing, resistance to, 97-99
 stitch tear, 98
 temper, 120-124
 temperature rise in sunlight, 119
 tensile strength, 86-97
 effect of acids on, 95, 118-119
 effect of location on, 88-90
 effect of relative humidity on, 90-91
 effect of splitting on, 95-97
 effect of variable factors, method for studying, 94-95
 ventilating properties, 102-110
 water absorption, 110-111
 wear resistance, 99-102
 sampling of, for chemical analysis,
 for microscopic examination, 65
 for tensile-strength tests, 88-90
 stuffing of, 26
 water-soluble matter in, nature of, 3, 31
 yield values, 131
Leaves, tanniferous, sampling of, 271
Leukanol, 311
Lime, analysis of, 234-241
 available, 235, 239
 composition of, 235
 hydrated, 234
 quicklime, 234
 total, in lime liquors, 251
Lime liquors, 219, 250-257
 analysis of, 234, 250-257
 constitution of, 219
 pH value of, 255
 plumping power, 255
Linseed mucilage, 430, 446
Linseed oil, 352, 448-454
 analysis of, 448-454
 boiled, 449, 453-454
 boiling of, control methods, 453-454
 raw, 452
 specifications for, 448
Liquid extracts, preparation for
 analysis, 281
 sampling, 272
 solution of, 274, 282
 specific gravity of, 296
Loading materials in leather, 33
Logwood, stain, 72
Lye (*see* Sodium hydroxide).
- M**
- Magnesia, in lime, 235
Magnesia mixture, preparation, 347
Magnesium, determination of, in
 leather, 17-20
 in lime, 237
 in sodium chloride, 222
 in water, 229
Magnifying power, 76-77, 79-81
Mangrove bark, analytical charge,
 285
 composition, 312
Mangrove extract, analytical charge,
 285
 sampling, 270
Matter insoluble in alcohol, in
 shellac, 440-441
 in soap (*see* Fillers).
Matter insoluble in benzene, in fats,
 371
Matter insoluble in carbon tetra-
 chloride, in carnauba wax, 439
Matter insoluble in ether, in mer-
 curic chloride, 225
Matter insoluble in water, deter-
 mination of, in albumins, 436
 in aluminum sulfate, 330
 in ammonium chloride, 258
 in barium sulfide, 246
 in calcium chloride, 249
 in chromium compounds, 321
 in dry bates, 261
 in oxalic acid, 428
 in pancreatin, 260
 mineral matter in, 261
 in potassium antimonyl tar-
 trate, 422
 in soap, 404
 in sodium carbonate and bicar-
 bonate, 345
 in sodium chloride, 220
 examination of, 221
 in sodium sulfide, 245

- Matter insoluble in water, determination of, in tanning materials, 275, 284, 287, 289
in water, 227
- Matter soluble in water, determination of, in albumins, 435-436
in leather, 3, 31-35
defining, difficulty of, 3
examination of extract, 34-35
"fixed," 268
in shellac, 445
in syntans, 311
in tanning materials, 275, 283, 287, 289
in water, 227
- Maumené value, 380
- Media (*see* Culture media).
- Melting point, A.L.C.A. method for, 358
capillary tube method for, 358
determination, in acetic acid, glacial, 441
in carnauba wax, 439
in fats, 358-359
in paraffin, 381-382
of fat in leather, relation to spew, 366, 374, 375
- Menhaden oil, constants of, 354
- Mercuric chloride, analysis of, 225
disinfecting agent, 219, 225
- Mercurous chloride, in mercuric chloride, 225
- Meta cresol purple, indicator, 199, 200
- Methyl orange, indicator, preparation, 26, 481
- Methyl red, indicator, for pH measurements, 199
for general purposes, 481
- Micrometer eyepiece, 79-81
- Microorganisms (*see* Bacteria).
- Microscope, 74-84
binocular wide-field, 84
- Microscopy, 65-85
dehydrating, 66
equipment for, 67-70, 73-84
fixing, 66
imbedding, 66
sampling, 65
- Microscopy, sectioning, 71
staining, 71-73
- Microtome, 67-70
freezing, 73-74
- Mimosa (*see* Wattle).
- Mineral acid, in leather (*see* Acid, mineral).
- Mineral matter, determination of, in albumins, 436
in bates, insoluble matter of, 261
in carnauba wax, 439
in casein, 431
in egg yolk, 408
in fats and oils, 371
in finishes, 447
in formaldehyde, 446
in lactic acid, 425
in leather, 13-15
analysis of, 15-23
soluble and insoluble, 14-15, 35
in linseed oil, boiled, 453
in mœllon dégras, 384
in oxalic acid, 428
in pancreatin, 260
in shellac, 446
in soap, 405
in sulfonated oil, 387
analysis, 392
in tanning materials, 297
in vulcanized oils, 456
- Mineral oil, analysis of, 380-382
detection, in fats, 372
in fat liquoring, 352
in stuffing and oiling leather, 26
- Mœllon dégras, 382-384
analysis of, 383-384
composition of, 383
extraction of, from leather, by diverse solvents, 27, 29
in fat liquoring, 26, 352
manufacture of, 382
- Moisture (*see* Water).
- Mounting sections, 71
- Mucilages, used in finishes, 430, 446
- Munson and Walker's table for glucose, 301-307

- Muriatic acid (*see* Hydrochloric acid).
- Mutton fat, constants of, 354
- Myrobalans, analytical charge, 285
- Myrobalans extract, analytical charge, 285
- composition, 312
- N
- Naphtha, analysis of (*see* Solvents).
determination of, in vulcanized oils, 454-455
- Neat's foot oil, cloud point of, 366
- constants of, 355, 356
- sulfonated, 26, 386
- used in fat liquoring, 26
- Neradol, 311
- Neutralization, in chrome tanning, 320, 325
- ionic theory of, 168
- Neutralizing agents, for chrome tanning, 320
- Nitrocellulose, analysis of, 457-461
- determination of, in leather, 49
- manufacture of, 456
- nitrogen content of, 456
- viscosity of, 457-460
- Nitrogen, determination of, in albumins, 436
- in bate liquors, 262-263
- in casein, 433
- in egg yolk, 411
- in finishes, 447
- by Kjeldahl method, 23-26
- in leather, 1, 23-26
- in lime liquors, 252-254
- in nitrocellulose, 460
- in pancreatin, 260
- in soaks, 233
- soluble, in soaks, 233
- volatile, in lime liquors, 252-254
- in soaks, 234
- Nitrophenol indicators, 199
- Non-albumin, soluble, in egg or blood albumin, 436
- Non-tannin, absorption of, by hide powder, 2
- Non-tannin, determination of, in leather extract, 34
- in tanning materials, 275, 284, 288, 289
- by Wilson-Kern method, 292-294
- ferrie chloride test for, 32, 291, 293
- sensitivity of, 295
- Non-volatile matter, determination of, in ammonia, 429
- in ammonium salts, 259
- in bates, 262
- in formaldehyde, 446
- in formic acid, 424
- in hydrochloric acid, 337
- in solvents for nitrocellulose, 463
- in sulfuric acid, 334
- Normal solution, defined, 474
- preparation of, 474-481
- Normality, 169, 170, 474
- O
- Oak bark, analytical charge, 285
- Oak-bark extract, analytical charge, 285
- for Wilson-Kern method, 292
- composition, 312
- Oak-wood extract, analytical charge, 285
- Objectives, 74, 76-78, 80
- Odor, residual, of solvents, 463
- Official methods, for bacterial counts, 138-144
- for leather analysis, 9-49
- for fat, criticized, 26-30
- for water-soluble matter, criticized, 31-34
- limitations of, 2
- for tannin analysis, 268-290
- criticized, 268, 285-289
- Oil-tanned leather, 48
- Oiling leather, 352
- Oils, constants of, 354-356
- fixed, non-drying, 352-380
- in lacquers, 472
- mineral, 352, 380-382
- sulfonated, 352, 384-395

- Oils, vulcanized, 352, 454-456
(*See also* Fats.)
- Olive oil, constants of, 355-356
 substrate for determining lipolytic activity of enzymes, 165
 used in making leather, 26
- One-bath chrome tanning, 320, 325
- One-bath chrome liquors, 325
- Osage extract, composition, 312
- Oxalate, determination of, in oxalic acid, 427
 in potassium antimonyl tartrate, 422
 in titanium potassium oxalate, 420
- Oxalic acid, analysis of, 427-428
 in formic acid, 425
 used in bleaching, 423
 in vegetable-tanned leathers, detection, 43
- Oxidized fatty acids (*see* Fatty acids, oxidized).
- Oxygen consumption of water, 230
- P**
- Palm kernel oil, constants of, 355
- Pancreatin, analysis of, 259-261
 as bating material, 257
 enzyme activity of, 153-167
- Paraffin, detection of, in carnauba wax, 438
 melting point of, determination, 381
 used in stuffing leather, 26
- Peanut oil, constants of, 355
- Perchlorate method for potassium, 421
- Permeability of leather, to gases, 107-110
 to water, liquid, 110
 to water vapor, 102-106
- Petrol ether, for fat analysis, 373, 374
 as solvent for leather fat, 3, 26-31
- pH value, 168-218
 calculation of, from E.M.F., 189-193
 definition of, 170-172
- pH value, effect of, on bacterial growth, 137
 on enzyme activity, 156
 on gelatin-salt test for tannin, 295
 on tannin analysis, 288
 measurement of, 168-218
 in bate liquors and solutions, 262-263
 in chrome liquors, 325, 327
 in colored liquids, 211, 214
 in culture media, 139
 by dilution method, 214
 in drenches, 264
 in fat liquors, 412
 by glass electrode, 196
 by hydrogen electrode, 173-194
 by indicator methods, 197-215
 in leather extracts, 39-43
 in lime liquors, 255
 by quinhydrone electrode, 195
 in soaks, 233
 in sulfonated oil emulsions, 395
 in syntan solutions, 313
 in tannin solutions and liquors, 300
 with colorimeter, 213
 in water, 229
 standardization, 193
- Phenol red, indicator, 199, 200, 211
- Phenolphthalein, indicator, preparation of, 36, 481
- Phosphate, determination of, in bates, 262
 in sodium phosphate, 347
- Phosphate buffers, 201-204, 207, 210
- Phosphorus, determination of, in casein, 432-433
- Pickle liquors, 338-339
- Pickling, 320, 338
- Picro-indigo-carmin, stain, 72
- Picro-red, stain, 72
- Pigments, in finishes, 430
 in lacquers, 457
 determination of, 472
- Pine bark, analytical charge, 285
- Pine-bark extract, analytical charge, 285
- Pipette, Dudley viscosimeter, 365

ANALYSIS OF LEATHER

- Plasticizers, 457, 461
 - Plating bacteria, 143
 - Platinizing electrodes, 175-177
 - Plumping power, measurement of,
 - by Wilson-Gallun method, 255
 - in lime liquors, 255
 - in tan liquors, 310
 - Poisoning, of electrodes, 175-176, 189, 193-194
 - by sulfide in lime liquor, 254
 - Polymerization, in boiling of linseed oil, 453
 - Porosity of leather, 107-110
 - Porpoise oil, constants of, 355
 - Potassium, determination of, by
 - chlorplatinate method, 421-422
 - by perchlorate method, 421
 - in titanium potassium oxalate, 420-422
 - in water, 229
 - separation of, from sodium, 421
 - Potassium antimonyl tartrate, analysis of, 422-423
 - manufacture of, 422
 - Potassium chloride, standard, preparation of, 479
 - Potassium chromate, indicator, preparation of, 481
 - Potassium dichromate, standard, preparation of, 480
 - Potassium hydrogen phthalate, buffers, 201-204, 207
 - standard for pH measurements, 193
 - Potassium hydroxide, alcoholic, preparation of, 378
 - Potassium iodide solution, reagent, preparation of, 450
 - Potassium permanganate, standard, preparation of, 230, 479-480
 - Potential, electrode, theory of, 173
 - Potentiometer, construction and operation of, 184-187
 - recording, 187
 - theory of, 180-184
 - Potentiometric method, for measuring pH value, 172-197
 - apparatus for, 174-188
 - Potentiometric method, for measuring pH value, compared with indicator method, 214
 - principle of, 173-174
 - procedure, with glass electrode, 196-197
 - with hydrogen electrode, 188-194
 - with quinhydrone electrode, 195-196
 - for titrating, tan liquors, 300
 - phosphates, 347
 - total acidity, 169, 215
 - Pour point of oils, 366-371
 - Precipitation figure of chrome liquors, 326-327
 - Proteins, in finishes, 430
 - determination of, 447
 - of skin, 1
 - Pycnometers, for liquids, 423
 - for solid fats, 357
 - Pyroxalin (*see* Nitrocellulose).
- R
- Quebracho extract, analytical charge, 285
 - Wilson-Kern method, 292
 - composition, 312
 - sampling, 270
 - Quebracho wood, analytical charge, 285
 - Quinhydrone electrode, 172, 195-196
 - applicable to syntans, 313

- Relative humidity, effect of, on
tensile strength of leather,
90-91
on water content of leather, 112
method for controlling, 104-105
Residue on evaporation (*see* Non-
volatile matter).
Resilience of leather, 124-128
Resinic acids (*see* Rosin).
Resins, in lacquers, 457
determination of, 472
Resolving power, 76-77
Resorcin-fuchsin, stain, 72
Rosin, detection of, in shellac, 443
determination of, in shellac, 443-
444
in soap, 396
- S
- Sal soda (*see* Sodium carbonate).
Salt (*see* Sodium chloride).
Salometer, 339
Salts, effect of, on bacteria counts,
145-150
Samples, preparation of, for analysis,
albumins, 434
chrome tanning compounds,
321
leather, 10-11
sodium sulfide, 242
tanning materials, 273, 280-
281
of tan liquors, preservation of, 272
of water for bacterial counts, 143
Sampling, of carnauba wax, 438
of leather, for chemical analysis,
8-11
for microscopic examination, 65
for tensile strength measure-
ments, 88-90
of sodium sulfide, 242
of solvents and diluents, 462
of tanning materials, 269-273
Sampling tube, for tanning extracts,
273
Saponification, of fats, 378-379
of waxes, 438
Saponification value, of fats and oils,
378-379
of linseed oil, 451
Sardine oil, constants of, 355
Saybolt viscosimeter, 360-365
Seal oil, constants of, 355
Sectioning, 71
Sediment, in oils, determination of,
371-372
Sesame oil, constants of, 355
Shark oil, constants of, 355
Sharpening agents in unhairing, 234
Sharpening microtome knife, 68-70
Shellac, analysis of, 439-446
in finishes, 430
determination of, 448
grades, 439
specifications for, 440
Silica, determination of, in leather,
16
in lime, 236
in sodium chloride, 221
in water, 228
Silver nitrate, standard, preparation
of, 479
Skins, raw, analysis of, 7
bacterial damage to, 136-137
bating of, 257
chrome tanning of, 320
curing of, 219
deliming of, 257
disinfection of, 219
fat content of, 26
microscopic examination of, 65-
85
dehydrating, 66
fixing, 66
nitrogen loss in soaking, 233
pickling of, 338
proteins of, 1
soaking of, 226
unhairing of, 234
Soak liquors, analysis of, 226, 232-
234
bacteria in, 144-145, 233
Soaking, 226
Soaking materials, analysis of, 226-
234

- Soap, analysis of, 397-406
 for alkali in fillers, 404
 free lye, 403
 total and combined, 401
 for chlorides, 405
 for fat, total, 398
 unsaponified, 398
 for fatty acids, examination of, 405
 total anhydrides, 399
 for fillers, 403-404
 for lye, free, 403
 for matter insoluble in water, 404
 for mineral matter, 405
 for rosin, 400
 for sulfate, 405
 for total soap, 402
 for unsaponifiable matter, 398
 for water, 397
 composition of, 397
 constitution of, 396
 in fat liquoring, 26, 352, 395-396
 specifications for, 396
Soap method, for hardness of water, 230
Soda ash (*see* Sodium carbonate).
Sodium, determination of, in calcium chloride, 250
 combined as soap, in sulfonated oil, 391
 in titanium potassium oxalate, 420-422
 separation of, from potassium, 420-422
Sodium bicarbonate, analysis of, 343-346
 composition of, 344
 determination of, in sodium carbonate and bicarbonate, 344-345
 in sodium thiosulfate, 340
 neutralizing agent in chrome tanning, 320
Sodium bisulfite, analysis of, 341-342
 composition of, 341
 determination of, in sodium thiosulfate, 340
Sodium bisulfite, determination of, in sulfites, 342
Sodium borate, tetra, analysis of, 346
 filler in soap, 396
 neutralizing agent in chrome tanning, 320
 preservative for egg yolk, 407
Sodium carbonate, analysis of, 343-346
 composition of, 344
 curing agent, 219
 determination of, in ash of egg yolk, 408
 in ash of sulfonated oil, 392
 in sodium bicarbonate, 344-345
 in sodium carbonate, 344-345
 in sodium hydroxide, 248
 in sodium sulfite, 343
 in sodium thiosulfate, 340
 filler in soap, 396
 neutralizing agent in chrome tanning, 320
Sodium chloride, analysis of, 220-224
 composition of commercial, 220
 determination of, in chromic chloride, 325
 in common salt, 223-224
 in egg yolk, 409
 in pickle liquors, 338
 in soap, 405
 in chrome tanning, 220
 in curing, 219
 in pickling, 220, 320, 338
 in soaking, 220
 specific gravity table, 339
 specifications for, 220
Sodium chromate, determination of, in sodium dichromate, 328-329
Sodium dichromate, analysis of, 327-329
 determination of, 327
 source of chromic salts, 321
 tanning with, 320
Sodium fluoride, antiseptic for soaking, 226
Sodium hydroxide, alcoholic, preparation of, 449
 analysis of, 248

- Sodium hydroxide, determination of, in carbonates, 344-345
in soak liquors, 234
in soap, 403
soaking agent, 326
in soap manufacture, 396
standard, preparation of, 475-479
for linseed oil analysis, 449
- Sodium hypochlorite, analysis of, 231
antiseptic for soaking, 226
- Sodium nitroprusside, indicator, preparation of, 243
- Sodium phosphate (di-), analysis of, 347-349
bating agent, 257
filler in soap, 396
neutralizing agent, in chrome tanning, 320
(tri-), analysis of, 347-349
- Sodium silicate, filler in soap, 396
- Sodium sulfate, analysis of, 225
curing agent, 219
determination of, in aluminum sulfate, 331
in chrome leather, 45
in chromium sulfate, 324
in soap, 405
in sulfonated oil, 390-392
- Sodium sulfide, analysis of, 241-245
composition of, 241
sampling, 242
soaking agent, 226
unhairing agent, 234, 241
- Sodium sulfite, analysis of, 341-342
determination, in sodium thiosulfate, 340
in sulfites, 342
reducing agent for chromate, 320-321
- Sodium thiosulfate, analysis of, 340-341
in chrome tanning, 320-321
standard, preparation of, 22, 450, 480
- Solidification point of fats, 359
- Solids, total, determination of, in albumins, 435
in finishes, 447
- Solids, total, determination of, in lacquers, 471
in syntans, 311
in tanning materials, 275, 282, 283
in water, 227
- Soluble matter (*see* Matter soluble in water, etc.).
- Solubility in water of titanium potassium oxalate, 419
- Solvents for nitrocellulose, 456-457
boiling point of, 469
ester value, 463-464
determination in lacquers, 472
distillation of, 463-470
sampling, 462
specifications for, 462
tests, 463-464
- Specific gravity, determination of, of acids, solutions, etc., 331-333, 335-337, 424, 425, 428
by barkometer, 296
of carnauba wax, 439
by displacement method, 131
of fats and oils, 356-357, 454
by flotation method, 439
by gravimeter, 296
by hydrometer, 331
of leather, 11, 130-131
of linseed oil, 450
by pycnometer, 357, 423
by salometer, 339
of solvents, 463
by Westphal balance, 356-357
- tables, ammonia, 429
hydrochloric acid, 336-337
formic acid, 424
sodium chloride, 339
sulfuric acid, 331-333
- Sperm oil, constants of, 355
- Splitting leather, effect of, on resistance to tear, 97
on strength and stretch, 95-96
on temper, 124
- Splitting machine, laboratory, 10, 55
- Spruce extract (waste sulfite liquor), analytical charge, 292
composition of, 312

- Stage, mechanical, 83
Staining, 71-73
Stains, microscopical, 72-73
Standard cell, 180-183
Standard solutions, preparation of, 474-481
Standards, for pH determination, indicator method, 201-204, 207
 potentiometric methods, 193
Starch, indicator, preparation of, 450, 481
Stearine, constants of, 355
Strength of leather (*see* Tensile strength).
Stretching, of leather, recovery after, 97
 resistance to, 86-97
Stuffing, 352
Substrate, 153-154
Sulfate, determination of, acid, in aluminum sulfate, 330
 in chrome leather, 44-46
 in chromium sulfate, 323-324
as barium sulfate, 223
chromium-bound, in chrome leather, 44, 46
combined with oil, in sulfonated oil, 390-391
in vegetable-tanned leather, 42-43
neutral, in chrome leather, 45
 in chromium sulfate, 324
protein-bound, in chrome leather, 44, 46
 (*See also* Sodium sulfate; Sulfur; Sulfuric acid.)
Sulfide, action of, on hair, 234
determination of, by evolution method, 242, 244
 by zinc method, 242, 243
poisoning of hydrogen electrode by, 193, 255
 (*See also* Sodium sulfide, etc.)
Sulfite cellulose, analytical charge, 285
test for, 277
Sulfites, analysis of, 341-343
 poisoning of hydrogen electrode by, 193
Sulfonated compounds, in sulfonated oil, 395
Sulfonated oil, 384-395
 analysis of, for alkali, combined as soap, 391
 total, 388
 for ammonia, 389
 for emulsion stability, 395
 for fat, neutral, 392, 394
 total, 392
 for fatty acids, combined, 388-389
 free, 388-389, 394
 for mineral matter, 387
 examination of, 392
 for pH value, 395
 for sulfate, 390-391
 for sulfonated compounds, 393-395
 for unsaponifiable matter, 387-388
 for water, 386
composition of, 386
extraction of, from leather, with diverse solvents, 27, 29-30
fat liquoring with, 26, 385
fractionation of, 393-395
manufacture of, 384-385
Sulfonic acid, detection of, in syntans, 313
 in vegetable leather, 38-44
Sulforicnoleic acid, 391
Sulfur, determination of, available in arsenic sulfide, 247
 free, in arsenic sulfide, 247
 total, in albumins, 436
 in casein, 433
 in leather, vegetable-tanned, 41-42
 in tanning materials, 299
 in vulcanized oils, 455
Sulfur chloride, 454
Sulfur dioxide, 341-343
 in manufacture of chromic salts, 320-321

- Sulfuric acid, analysis of, 331-334
 composition of, 331
 determination of, in chrome-tanned leather, 44-46
 in lactic acid, 425
 in pickle liquors, 339
 in syntans, 313
 in vegetable leather, 37-44
 in vitriol, 331, 334
 in pickling, 338
 specific gravity table, 332-333
 standard, preparation of, 450, 475-479
 uses in tannery, 331
- Sulfurous acid, 341-343
- Sumac extract, analytical charge, 285
 for Wilson-Kern method, 292
 composition, 312
- Sumac leaves, analytical charge, 285
 for Wilson-Kern method, 292
 composition, 312
- Suspended matter, determination of, in water, 227
- Syntans, analysis of, 311, 313
 analytical charge, 285
 effect of, on determination of mineral acid in leather, 38, 43, 48
- Tallow, constants of, 355
- Tallow soap, composition of, 397
- Tan liquors, analysis of, for chlorides, 298
 for lime, 298
 for mineral matter, 297
 for pH value, 300
 by colorimeter method, 213
 for plumping power, 310
 for specific gravity, 296
 for tannin, 269, 276-277, 294, 297
 by Wilson-Kern method, 294
 sampling of, 272
- Tannin, compound with hide substance, 290
 hydrolyzability of, 31-33, 290-291
- Tannin, constitution of, unknown, 2
 content of extracts, etc., 312
 definition of, 290
 determination of, 2, 267-268
 in leather, 48-49
 in leather extract, 34
 in tanning materials, 267-318
 by A. L. C. A. method, 273-277
 by International method, 278-285
 by other methods, 295
 by Wilson-Kern method, 290-295
 gelatin-salt test for, 290, 293
 sensitivity of, 295
 (See also Tanning materials.)
- Tanning, definition of, 7
- Tanning agent, determination in leather, 8
- Tanning materials, vegetable, analysis, 2, 267-319
 for acidity, total, 277, 300
 agreement between analysts, 273, 284
 by A. L. C. A. method, 268-278
 apparatus for, 277-278, 295
 calculation of tannin, 289-290
 for chlorine, 299
 detannization, 2, 267, 268, 275, 284, 287, 293
 dishes, 277, 278
 drying, 277, 278, 286, 294
 evaporation, 277, 278, 286
 extraction, 274, 281, 285
 filtration, 275, 284, 287, 292
 for glucose, 299, 301-307
 hide powder for, preparation of, 275, 280, 283, 288, 292
 for insoluble matter, 275, 284, 287, 289, 292
 by International method, 268, 278-285
 for mineral matter, 297-299
 for non-tannin, 275-276, 284, 287, 289, 294
 for pH value, 300

- Tanning materials, vegetable, analysis, pH value, effect on tannin determination, 288
for plumping power, 310
purposes of, 267-268
reagents, 275, 279-280
for solids, total, 275, 282-283, 289, 292
for soluble matter, 275, 283, 289, 292
solutions, preparation of, 274-275, 281-282, 285, 286, 292
for specific gravity, 284, 296-297
for sulfite cellulose, 277
for sulfur, 299
for tannin, 2, 276, 284, 289, 292-294
for water, 274, 275, 282, 289
by Wilson-Kern method, 268,
color of, 300, 307-310
composition of, 310, 312
extraction, commercial, 267
for analysis, 274, 281
extracts, sampling of, 269-273
solution of, 274-275, 281-282, 292
identification of, 295
liquors (*see* Tanliquors).
raw, extraction of, 274, 281, 285
sampling of, 271
sampling of, 269-273, 280-281
spent, sampling of, 272
Tartar emetic (*see* Potassium antimonyl tartrate).
Tartaric acid, detection in potassium antimonyl tartrate, 422
Tearing, resistance of leather to, 97-99
stitch tear, 98
Temper of leather, 120-124
Temperature corrections, for barkometer, 296
for E.M.F. of calomel electrode, 189-190
Temperature rise of leather in sunlight, 119
Tensile strength of leather, 86-97
Thermal value (*see* Maumené value).
Thermometers, for cloud and pour point, 367-368
for distillation, 467
for melting point, by A.L.C.A. method, 358
for melting point of paraffin, 381
for Saybolt viscosimeter, 362-363
Thymol, antiseptic for tan liquor samples, 272
Thymol blue, indicator, 199-200, 211
Tinctorial power of dyes, 417
Tintometer, Lovibond, 300
Titanium, determination of, in leather, 15, 18
in titanium potassium oxalate, 419
Titanium potassium oxalate, analysis of, 418-422
composition of, 418
as mordant, 418
Titer test, 359
of fatty acids from soap, 406
Tizerah, analytical charge, 285
Toluene, for testing nitrocellulose, 458
Toluene distillation method for water, 12-13, 371
Trypsin, 153-154
unhairing action, 234
Two-bath chrome tanning process, 320
- U
- Ultra-filtration of tannin solutions, 295
Unhairing, 234
Unhairing materials, 234
analysis of, 234-257
Unoxidized fatty acids (*see* Fatty acids).
Unaponifiable matter, determination of, in fats, 372-374
in linseed oil, 451
in soap, 398-399
in sulfonated oil, 387-388
in waxes, 437-438
Unaponified fat, in soap, 396, 398

V

- Valonea, analytical charge, 285
composition of, 312
sampling, 270
- Vegetable tanning materials (*see*
Tanning materials).
- Ventilating properties of leather,
102-110
- Viscols, 454-456
- Viscosimeters, air bubble, 365
capillary, 459
Dudley pipette, 365
falling ball, 457
Saybolt, 360-365
- Viscosity, determination of, in casein
solutions, 434
in nitrocellulose solutions, 457-
460, 472
in oils, 359-365
in vulcanized oils, 454
- Vitriol (*see* Sulfuric acid).
- Voltage (*see* Electromotive force).
- Vulcanized oils, analysis of, 454-456
manufacture of, 454
for oiling leather, 26, 352

W

- Walpole technic, 205, 211
- Water, analysis of, 227-231
bacteriological examination of,
138-144
determination of, in albumins, 434
in casein, 431
in egg yolk, 408
in fats and oils, 371
by gasoline miscibility test, 463
in leather, 11-13
in lime, 240
in moellon dégras, 383
in pancreatin, 260
in shellac, 444
in soap, 397-398
in sodium carbonate, 343
in sodium chloride, 220
in solvents, 463
in sulfonated oil, 386

- Water, determination of, in:
materials, 274-275, 282, 289
by toluene distillation method,
12-13, 386-387
hardness, of, 230
mechanical, in hydrated lime, 240
requirements of, for tannery use,
226
- Water absorption of leather, 110
- Water content, of hide powder, pre-
scribed, 276
of leather, effect of, on resilience,
125
on tensile strength, 90-91
variation of, with relative hu-
midity, 112
- Wattle bark, analytical charge, 285
- Wattle extract, analytical charge,
285
for Wilson-Kern method, 292
composition of, 312
sampling, 270
tannin content of, 268
- Wax, determination of, in finishes,
448
in shellac, 444
- Waxes, analysis of, 437-439
constants of, 437
in finishes, 26, 430
hydroxyl value of, 379
- Wear resistance of leather, 100-102
- Westphal balance, 356-357
- Whale oil, constants of, 355
- Wilson-Kern extractor, 35, 293
- Wilson-Kern method for tannin
analysis, 268, 290-295
detannization, 293
effect of time of washing, 291-
292
losses, detection of, 294
preparation of hide powder, 292
of solutions, 292
for syntans, 311
for tan liquors, 294
- Woods, tanniferous, extraction of,
274
sampling, 271, 280
tannin content of, 311

Wool fat, constants of, 355

in mœillon dégras, 382

Working cell, 182-183, 185

Y

Yield values of leather, 131

Z

Zinc salts, as antiseptics for soaking
226

Zinc sulfate, standard, preparation
of, 243

